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1994

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Secţia II
CHIMIE ŞI INGINERIE CHIMICĂ

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CYCLIC VOLTAMMETRY OF *para*-AMINOPHENOL
SYNTHETIC REAL SAMPLES

BY
DOINA BEJAN and AL. DUCA

1. Experimental

a) *p*-Aminophenol (*p*AF) solution synthetical sample (5.6×10^{-2} M) prepared with twice distilled water.

b) 10^{-1} M Na_2SO_4 solution prepared with analytical grade substance and twice-distilled water.

c) Paste carbon electrode (P.C.E.) prepared as described in [1],...,[3].

The recordings of the cyclic voltammograms made on an Polarograph OH-102 Radelkis were obtained according to [1], [4].

2. Results and Discussion

References on the electrochemical behaviour of *p*AF are to be found in [4].

By extending our studies on a synthetic sample of purified *p*AF within the $2.5 \times \times 10^{-4}$ ... 2.25×10^{-3} mol.l^{-1} concentration range, its electrochemical behaviour, the influence of some factors (potential scanning rate, concentration of the depolarizer), as well as the nature of the voltammetric currents could be settled.

The general shape of the cyclic voltammogram is somewhat different from that of the standard *p*AF under the same conditions. The characteristics of the cyclic voltammogram for a concentration closed to that of the standard sample (1.68×10^{-3} mol.l^{-1}) are given in Table 1.

In comparison with the standard *p*AF, the cyclic voltammogram of the purified sample shows new anodic peaks or slight shiftings of the potentials of the peaks present in the standard voltammogram, probably due to the presence of some associated forms and of products resulting by the partial oxidation of *p*AF.

Based on the parameters ΔE, [V], and ip_a/ip_c, the electrochemical process of *p*AF might be appreciated to contain a stage of irreversible oxidation within the +0.750 ... + 0.680 V domain, as well as partially reversible processes in which either electrooxidation or electroreduction prevail (s. Table 1). The kinetics of the electron exchange is middle-slow ($\Delta E = 0.180$ ... 0.400 V).

Table 1

Voltammetric Characteristics of Purified pAF (P.C.E.; Na_2SO_4 10^{-1} M; $C = 1.68 \times 10^{-3}$ mol.l^{-1}; $S = 2 \times 10^{-7}$ A/div.; $v = 50$ mV/s)

Potential domain, [V]	Anodic peaks		Cathodic peaks		ΔE_p, [V]	ip_a/ip_c
	Ep_a, [V]	ip_a, [μA]	Ep_c, [V]	ip_c, [μA]		
0.0 → +1.4	+0.300$^{(1)}$	3.80	(+0.480$^{(3)}$)	(0.40)	0.270$^{(1)}$	0.792$^{(1)}$
+1.4 → −0.7	+0.560$^{(2)}$	7.00	+0.160$^{(2)}$	4.20	0.400$^{(2)}$	1.670$^{(2)}$
(cycle *a*)	+0.750$^{(3)}$	6.30	+0.030$^{(1)}$	4.80	0.270$^{(3)}$	15.750$^{(3)}$
	–	–	−0.170	6.60	–	–
	(−0.170)	(0.60)	(+0.500$^{(4)}$)	(0.40)	0.240$^{(1)}$	0.362$^{(1)}$
+1.4 ⇌ −0.7	+0.070$^{(1)}$	2.50	+0.160$^{(3)}$	4.20	0.210$^{(2)}$	0.708$^{(2)}$
(cycle *b*)	+0.240$^{(2)}$	3.40	+0.030$^{(2)}$	4.80	0.320$^{(3)}$	1.080$^{(3)}$
	+0.500$^{(3)}$	5.20	−0.170$^{(1)}$	6.90	0.180$^{(4)}$	10.500$^{(4)}$
	+0.680$^{(4)}$	4.20	–	–	–	–

Obs. *a* – The correspondence of the anodic–cathodic peaks is approximate;
b – Numbers 1, 2, 3, 4 represent the corresponding anodic–cathodic peaks of voltammogram.

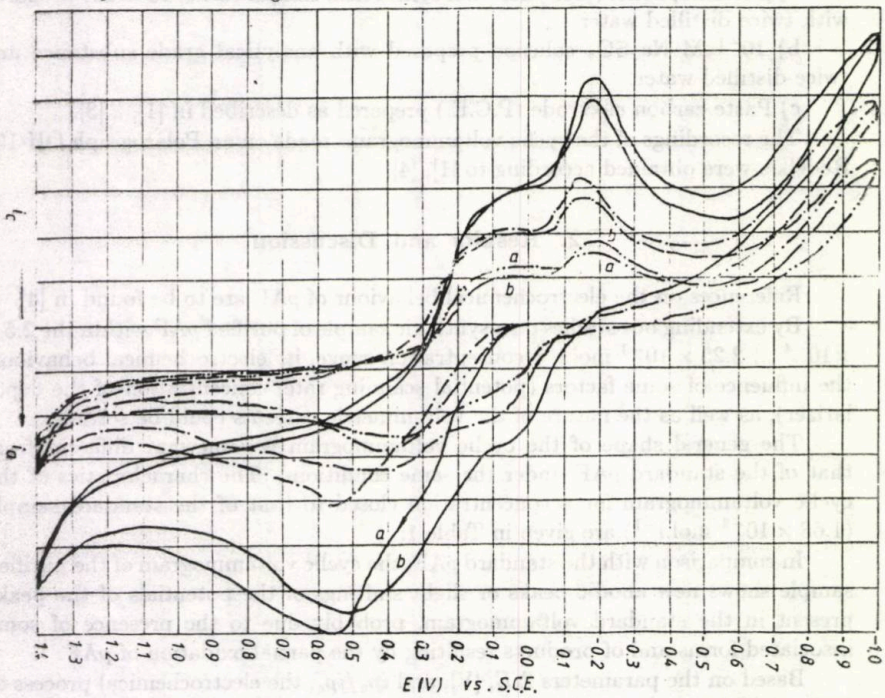

Fig. 1.– Cyclic voltammogram of *p*AF (synthetic sample). Influence of *p*AF concentration on voltammetric currents intensity (P.C.E.; Na_2SO_4 10^{-1} M; $v = 50$ mV/s; $S = 2 \times 10^{-7}$ A/div.; $-1.0 \rightleftharpoons +1.4$ V potential domain with respect to S.C.E.); ——— 1.68×10^{-3} M, – · – 1.12×10^{-3} M, – · · – 0.56×10^{-3} M.

By taking into account the very intense peak in the cycle a ($Ep_a = +0.380$ ... ... $+ 0.550$ V) and the correspondent anodic – cathodic peaks ($Ep_a = +0.070$ ... ... $+ 0.040$ V and $Ep_c = -0.170$ ... $- 0.200$ V), the influence of the depolarizer concentration on the intensity of the voltammetric currents was studied.

The function i_p vs. c was found to be linear for all the mentioned potential values, which indicates the diffusional character of the electrode process (Figs. 1 and 2). This fact is also supported by the slope values of the function $\lg i_p$ vs. $\lg v$, for both anodic and cathodic currents ($\tan \alpha \simeq 0.50$, a proper value of the diffusion current – Figs. 3 and 4).

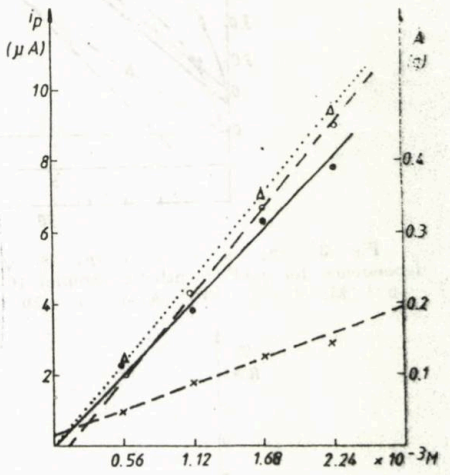

Fig. 2.– ip vs. C and A(g) vs. C dependence of pAF (synthetic sample). (P.C.E.; Na_2SO_4 10^{-1} M; $v = 50$ mV/s; $S = 2 \times 10^{-7}$ A/div.; $-1.0 \rightleftharpoons +1.4$ V potential domain with respect to S.C.E.); $\cdots\Delta\cdots$ ip_a (cycle a); —×— ip_a (cycle b); —o— ip_c (cycle b); —•— A(g).

The dependence of the anodic and cathodic voltammetric currents on the potential scanning rate is depicted in Figs. 3 and 4.

According to literature [5], this type of i_p vs. v dependence is characteristic for irreversible redox reactions on the electrode surface, when the compound is present as a monolayer.

The plotting of the i_p vs. $v^{1/2}$ function was linear for both reduction and oxidation (Figs. 3 and 4). In this case, the semiinfinite diffusion of the electrochemical charge represents the prevailing phenomenon.

3. Conclusions

The pAF real samples may be characterized by cyclic voltammetry on carbon electrodes (P.C.E.) with 10^{-1} M Na_2SO_4 as support electrolyte, within the -1.0... ... $+ 1.4$ V potential domain, with respect to S.C.E.

The purity of synthetic samples may be estimated qualitatively by the comparison of their voltammetric characteristics with those of the standard pAF.

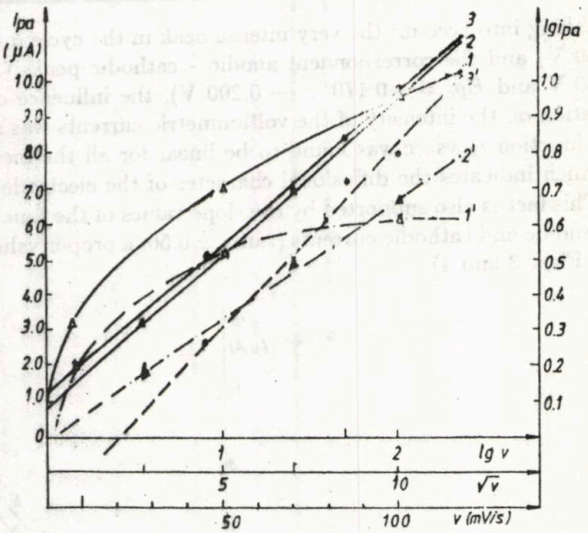

Fig. 3.– ip_a vs. v (*1,1'*), ip_a vs. $\sqrt{v}$ (*2,2'*) and $\lg ip_a$ vs. $\lg v$ (*3,3'*) dependence for *p*AF (synthetic sample) ($C = 5.6 \times 10^{-4}$ mol/l^{-1}; P.C.E.; Na_2SO_4 10^{-1} M; $S = 2 \times 10^{-7}$ A/div.; $v = 50$ mV/s); —— cycle *a*; – – – cycle *b*.

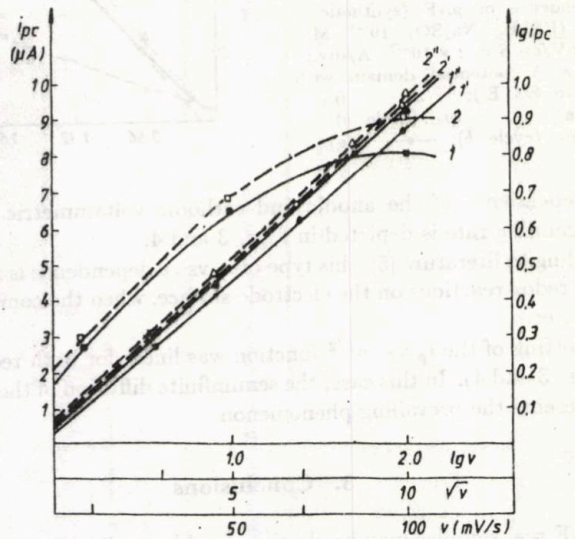

Fig. 4.– ip_c vs. v (*1,2*), ip_c vs. v (*1',2'*) and $\lg ip_c$ vs. $\lg v$ (*1'',2''*) for *p*AF (synthetic sample) ($C = 5.6 \times 10^{-4}$ mol/l^{-1}; Na_2SO_4 10^{-1} M; $S = 2 \times 10^{-7}$ A/div.); —— cycle *a*; – – – cycle *b*.

The electrochemical behaviour of the synthetic samples under study, very close to that of the standard *p*AF, is indicative of a synthesis process very well performed.

The following of the synthesis process development as well as its optimizing may be suggested to be performed by cyclic voltammetry.

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VOLTAMETRIA CICLICĂ A *para*-AMINOFENOLULUI
Probe reale sintetice

(Rezumat)

Pe baza rezultatelor obţinute în cercetarea comportării electrochimice a *p*AF pur (etalon) s-a întreprins un studiu asupra unor probe reale, sintetice, de *p*AF.

Obiectivele urmărite constau în caracterizarea acestora prin voltametrie ciclică pe electrod pastă de cărbune, evidenţierea influenţei unor factori şi stabilirea naturii proceselor electrodice ce au loc.

Utilizând caracteristicile voltametrice ale probelor reale poate fi estimată calitativ puritatea lor şi pot fi obţinute informaţii asupra corectitudinii procesului de sinteză.

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ULTRAVIOLET AND ATOMIC ABSORBTION SPECTROPHOTOMETRIC MICRODETERMINATION OF LEAD IN ORGANOLEAD COMPOUNDS AND IN GEAR OIL SAMPLES AFTER OXYGEN FLASK COMBUSTION

BY

M. E. M. HASSOUNA

1. Introduction

Organic lead compounds have been used since 1923 as additives to petrol for increasing the octane rating of fuels for use in high compression internal combustion engines, besides their various industrial uses [1]. Most of methods advocated for the determination of their lead content comprise a method of decomposition and another of finish. B e l c h e r et al. [2] reported the difficulty encountered in applying the oxygen flask method for the decomposition of Pb-containing organic compounds; Pb alloys with the Pt sample holder leading to low recoveries.

The present method depends on the combustion of organolead compounds in 10 ml 1:1 HCl soln. in an oxygen flask fitted with a silica spiral as sample holder. Samples of gear oils are also combusted on the semi-micro scale in larger flasks. Combusted samples are determined in the UV region and by AAS. Comparative complexometric titrations using both visual and potentiometric end point detection are parallely done.

2. Apparatus and Reagents

2.1. Apparatus

Microanalytical balance, E. M e t t l e r (M5).

Oxygen flasks, 500, 750 and 1000 ml conical flasks of which their stopers are made of silica provided with a silica spiral (5 turns) resembling that advocated by B e l c h e r et al. [3].

Spectrophotometer, recording with graphic printer, UV 240, 190...900 nm and 1 em quartz cells, Shimadzu corporation, Kyoto, Japan.

Atomic absorption spectrophotometer, Perkin-Elmer 2380.

Electronic potentiometer, Sargent-Walch, IL., USA with standard calomel and mercury electrodes assembly.

2.2. Reagents and Materials

Standard lead solns.: for UV made by dissolving the appropriate weight of AR lead chloride in 6M HCl soln. 1000 ppm soln. in Pb prepared from $Pb(NO_3)_2$ in water containing some nitric acid.

EDTA soln., 0.01 M & 0,005 M solns. of the disodium salt in water.

Sodium acetate–acetic acid buffer.

Xylenol Organe indicator: 0.5% aqueous soln.

Ethanol–hexane mixture, prepared by mixing equal volumes.

3. Procedure

3.1. Combustion of Organolead Compounds

Weigh exactly 3..5 mg of the sample in the ashless filter paper. Fix it in the silica spiral. Charge the 500 ml flask with 10 ml 1:1 HCl. After combustion, transfer quantitatively with 6M HCl to 50 ml volumetric flask. Measure the absorbance at 270 nm. Concentrations are determined in the range 0.5...40 ppm (Figs.1 and 2).

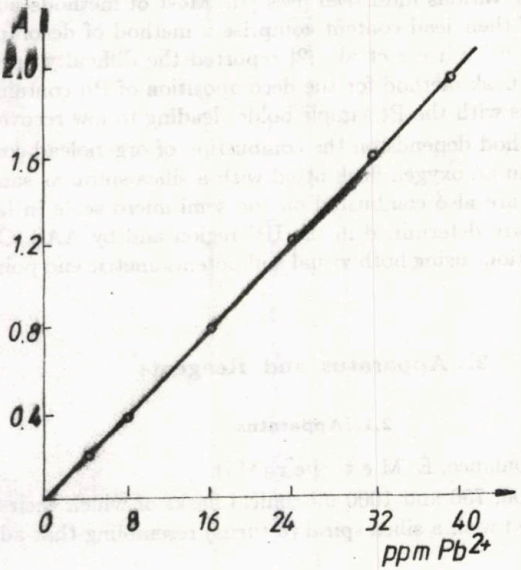

Fig. 1.– Calibration curve.

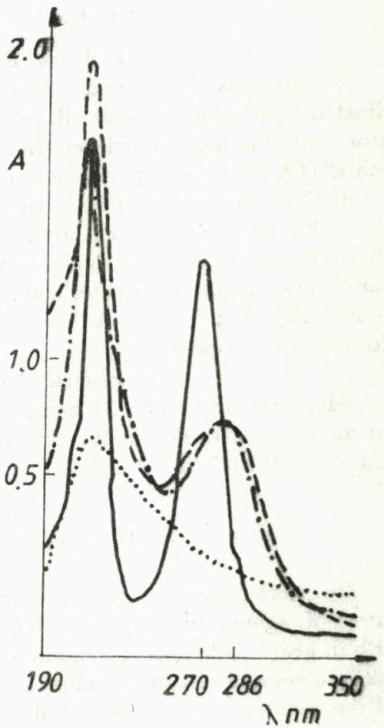

Fig. 2.– Pb^{2+} – chlorocomplex in 1:1 HCl: ··· blank; —— pure organic Pb compounds; - - - S or P contg. compounds; -·-·- gear oil sample.

3.2. The AAS Procedure

a) *For organolead compounds.* Weigh accurately 3...5 mg of the compound. Combust in a 500 ml flask charged with 10 ml 1:1 HCl. After combustion, transfer with water to 50 ml volumetric flask. 5 ml aliquot is further diluted to 50 ml with water. Aspirate the latter soln. in the atomic absorption spectrophotometer using the hollow cathode lamp for lead at the line 217.0 nm, under the following conditions: Slit (0.07 nm) with relative noise (1.0) and high sensitivity of 0.19 mg/l; recommended flame is Air–Acetylene, air flow 55, fuel flow = 30, gas pressure (regulater) = 0.47, operating current = 12 mA.

Concentrations are determined by reference to a calibration curve covering the range 0.5...20 ppm.

b) *For gear oil samples.* Weigh by difference, sample weights in the range 20...25 mg using a micro syringe or a capillary. Combust in a 750 ml oxygen flask charged with 20 ml 1:1 HCl. Transfer to 50 ml volumetric flask with water. 5 ml aliquot is diluted to 50 ml and is aspirated in the aparatus under the same specific conditions.

3.3. The Complexometric Check

a) *Visual End Point Detection*

i) Organolead compounds. To an aliquot (10 ml) of the sample (step **2.2** a), adjust the pH with ammonia till pH=4. Add 2...3 drops of Xylenol Orange indicator, and solid hexamethylenetetramine till red violet colour (pH= 5...6). Titrate with EDTA till the sharp change to lemon-yellow.

ii) Gear oil samples. Due to their low Pb content, semi micro weights in the range 100...130 mg of the oils are used. A 1 litre flask charged with 20 ml of 25% HNO_3 (Merck) is used for combustion. Combustion products are evaporated till near dryness. Dilute with water and repeat the evaporation and dilution to remove the majority of nitric acid. Adjust the pH and titrate in the same flask exactly as with org. Pb compounds.

b) *Electric End Point Detection* [4]

Adjust the pH to 4.6 with hexamine powder. Connect the assembly of calomel and mercury electrodes to the electronic potentiometer. Stirr magnetically and titrate with 0.0025 M EDTA soln.

4. Results and Discussion

This work presents easy and rapid methods for the determination of the lead content of organolead compounds. The methods are applied for the determination of Pb in gear oils known to contain as low as 0.1...0.3% Pb. A variety of oxygen flask volumes and absorption solns. are used to suit the different natures of samples and the quantities to be determined. Silica spiral is used as the sample holder due to alloy formation of Pb with Pt.

Applying the procedure of shaking the gear oil samples with a mixture of n-hexane–ethanol and extraction of lead carboxylates in 1:1 HCl soln. [5], results were approximately one tenth of those obtained after oxygen flask combustion. This reflects the potentiality of the oxygen flask method in the eliberation of the total Pb^{2+} content. For convenience, the methods of finish are discussed below.

a) *The ultraviolet method.* $PbCl_2$ in 1:1 HCl has a good peak at 270 nm. The use of 1:1 HCl soln. as absorbent providing the chloride complex ready for direct measurement in the UV without further treatment. although the method is simple and raid, it suffers many interferences. All ions known to absorb in the UV in 1:1 HCl must be absent. The contamination with sulphur shifts the absorption maximum towards a longer wavelength by about 6...8 nm appearing at 278 nm with an appreciable reduction of the optical density. This explains the appearance of the absorption maxima of gear oils samples. This is not unexpected since most of petroleum compounds are sulphur containing. Compound No.10 in Table 1 contains P, S and Pb; its absorption maximum appears at 276 nm (Fig.2). The analysis of three sulphur-containing org. Pb compounds gave inconsistent low recoveries.

In the present work, besides the combustion of 11 org. Pb compounds gear oil

Table 1

Microdetermination of Lead in Organolead Compounds by UV and Atomic Absorption Spectrophotometry.

No.	Compound & Formula	% Pb				
		Calcd.	UV method		A.A.S. method	
			$\bar{x}$	s	$\bar{x}$	s
1.	Lead oxalate (C_2O_4Pb)	70.19	69.79	0.440	70.53	0.396
2.	Lead tartrate ($C_4H_4O_6Pb$)	58.32	57.81	0.419	57.96	0.394
3.	Lead salicylaldoximate ($C_7H_5O_2NPb$)	60.53	61.06	0.477	60.10	0.432
4.	Lead citrate ($C_{12}H_{16}O_{17}Pb$)	58.98	58.46	0.477	58.98	0.468
5.	Lead acetate ($C_4H_{12}O_7Pb$)	54.62	54.03	0.437	54.23	0.399
6.	Lead tetraphenyl ($C_{24}H_{20}Pb$)	40.18	40.48	0.323	39.97	0.224
7.	Lead oxinate ($C_{18}H_{12}O_2N_2Pb$)	41.82	42.12	0.393	41.56	0.346
8.	Dilead tetraoxalylurea ($C_9O_{13}N_2Pb_2$)	54.63	54.12	0.476	54.25	0.386
9.	Lead piperidine dithiocarbamate ($C_{12}H_{20}N_2S_4Pb$)	39.26			38.89	0.370
10.	Lead O,O-diethyl-dithiophosphate ($C_8H_{20}O_4S_4P_2Pb$)	37.90			38.13	0.337
11.	Dilead tetraoxalylthiourea ($C_8O_{12}N_2SPb$)	53.50			53.81	0.451

samples are subjected to oxygen flask combustion, for the first time. Metals such as Zn, Cd, Co and Hg known to form coloured complexes with Xylenol Orange at pH=5; the presence of any of them may affect both the UV and the complexometric titrations methods. Potentiometry provides clear-cut end points and higher degree of selectivity. This necesitated the combustion of semi micro amounts of the oils.

Table 2

Analysis of Gear-Oil Samples After Oxygen Flask Combustion by Complexometry and Atomic Absorption Spectrophotometry.

Gear-Oil Source	The Complexometric method			The A.A.S. method	
	Weight range	% Pb		Weight range	% Pb
	mg	Visual	Potent.	mg	
Co-op Co.	126.89...	0.263...	0.271...	15.75...	0.261...
	127.31	0.290	0.304	24.46	0.298
Esso Co.	116.37...	0.150...	0.148...	20.20...	0.150...
	124.275	0.172	0.169	20.90	0.190
Mobil Co.	107.05...	0.090...	0.095...	14.74...	0.093...
	114.02	0.103	0.100	19.06	0.121
Misr Petroleum Co.	125.49...	0.139...	0.137...	20.09...	0.135...
	125.93	0.144	0.140	20.20	0.147

b) *The A.A.S. method.* Several workers reported the direct determination of Pb in gasoline by A.A.S. [6],...,[12]. Some workers [11], [12] added Aliquat 363 to stabilize the response of the diiodolead compounds. This problem has no presence in the present work since Pb is aspirated in the A.A.S. as $PbCl_2$.

Rauret et al. [13] combusted atmospheric particulate matter, after adsorption on a cellulose filter in the oxygen flask using 10% HNO_3 soln. as absorbent. The A.A.S. method is remarkably free from interferences. Sulphur contamination cause no interferences (compounds 9...11, Table 1). The analysis of gear oil samples from four egyptian companies are illustrated in Table 2. This work is considered as an extension of our interest in the microanalysis of org. Pb compounds [14].

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MICRODETERMINAREA PLUMBULUI PRIN SPECTROSCOPIE ÎN ULTRAVIOLET ŞI ABSORBŢIE ATOMICĂ DIN COMPUŞI ORGANICI ŞI ULEIURI DE UNGERE DUPĂ COMBUSTIE ÎN FLACON CU OXIGEN

(Rezumat)

Au fost supuşi combustiei în atmosferă de oxigen 11 compuşi organici cu plumb, folosind ca absorbant 10 ml HCl 1:1 şi ca suport pentru probă o spirală de cuarţ. Conţinutul de plumb din probă s-a determinat prin spectroscopie în ultraviolet şi absorbţie atomică. Probele de uleiuri, provenite de la patru companii egiptene, după combustie în flaconul de oxigen, au fost absorbite în 20 ml HNO_3 25%, iar produsul s-a determinat prin absorbţie atomică, complexonometrie şi potenţiometric.

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ANALYSIS OF TECHNICAL TEREPHTHALOYL DICHLORIDE BY A TITRIMETRIC METHOD

BY

MIOARA SURPĂŢEANU and MARIA GĂBURICI

1. Introduction

Terephthaloyl dichloride is an important intermediate in aromatic polyamides synthesis. The ground source of raw material for terephthaloyl dichloride is the terephthalic acid. Due to its reaction with thionyl chloride, the crude reaction product, beside chlorated compounds of terephthalic acid, could contain the unreacted acid. It is not avoid the presence of hydrochloride acid.

In this paper two purposes are proposed: the selection of an efficacious, available dissolution medium and the finding of a method of analysis for the compounds in reaction mixture.

2. Experimental

During the laboratory experiments, the following reactives have been used: terephthalic acid (TFA) Merck; dimethylformamide (DMF) Merck; dioxane; fresh distilled aniline; aqueous solution NaOH 0.1 N; aqueous solution $AgNO_3$ 0.1 N; aqueous solution NH_4SCN 0.1 N; aqueous solution bromothymol blue (ABT) 0.1%; aqueous solution ferric-ammonium sulphate 40%.

In literature [1], the mixture dioxane – water (3:2, v/v) as solving medium for carboxylic acids and their halogen derivates has been indicated. There are also mentioned some titrimetric methods for chloride acids analysis in non-aqueous medium. For this purpose there are used some different solvent mixtures: diethylether – – chlorobenzene [2], benzene – methanol [3], etc. In titration, a NaOH solution [1] or sodium metoxide in methanol – benzene and tributylamine in dioxane [4],...,[6] are recommended.

2.1. Solvent Selection

The previous indicated solvents are not suitables in the dissolution of the samples containing terephthalic acid and terephthaloyl dichloride. From the tried

solvent systems, the best results with dioxane – DMF – water and DMF – water in various ratios have been obtained. We are decided for this last solvent mixture because dioxane presents a certain acidity. It is necessary in view to operate the corresponding correction.

In order to establish the available method for determination of all compounds in reaction mixture, we analysed several experimental samples.

These samples contain only pure terephthalic acid, technical terephthaloyl dichloride as well as mixtures of terephthalic acid and terephthaloyl dichloride in different ratios with or without hydrochloride acid.

2.2. Terephthalic Acid Analysis

Terephthalic acid has been determined by neutralization with NaOH solution as follow:

$$(1) \quad HOOC - C_6H_4 - COOH + 2NaOH = NaOOC - C_6H_4 - COONa + 2H_2O$$

The titration has been realized in the presence of bromothymol blue as indicator.

A known sample of acid (0.05...0.11 g) is solved in 10 ml DMF and diluted with 20 ml water. Then, in presence of ABT (5 drops) the sample is titrated with standard solution NaOH to appearence of a blue colour. The obtained results are given in the Table 1.

Table 1

Analysis of Terephthalic Acid

No.	Sample weight, [g]	Consumed NaOH, [mmoles]	%TFA
1	0.0538	6.502	100.31
2	0.0508	6.096	99.60
3	0.0508	6.132	100.18
4	0.1010	12.142	99.78
			99.97

When the sample is solved in the mixture dioxane – DMF – water the end-point of titration is difficult to establish because there are observed many green tints. If the mixture of solvents is formed only by DMF – water, the sharpest change in indicator colour will occur. This assures a best reproduction of the obtained values.

When a mixture dioxane – water is used we observed that is necessary to correct the consumption of NaOH volume. This correction due to acidity of dioxane is a function of dioxane ratio in the solvent mixture.

Experimentally, we established that in the presence of ABT, 0.025 mmoles NaOH is consumed by 1 ml dioxane.

2.3. Analysis of Technical Terephthaloyl Dichloride

The determination of terephthaloyl dichloride is based on its hydrolysis and neutralization of the obtained compounds as follow:

(2) $ClOC - C_6H_4 - COCl + 2H_2O = HOOC - C_6H_4 - COOH + 2HCl$

(3) $HCl + NaOH = NaCl + H_2O$

and (1).

If it is accepted that technical terephthaloyl dichloride even contains free carboxylic groups, in order to realize their discrimination, the determinations on the parallel samples have been imposed.

In the first sample the total acidity due to –COCl and –COOH groups is titrated. The following reactions take place:

(4) $-COCl + H_2O = -COOH + HCl,$

(3) and

(5) $-COOH + NaOH = -COONa + H_2O$

A second sample is treated with aniline in order to avoid the hydrolysis of –COCl groups:

(6) $-COCl + 2C_6H_5NH_2 = -CONHC_6H_5 + C_6H_5NH_2.HCl$

After that, aniline hydrochloride arrising in reaction (6) with free carboxylic groups, using NaOH solution, are neutralized as follow:

(7) $C_6H_5NH_2.HCl + NaOH = C_6H_5NH_2 + NaCl + H_2O$

The accurately weighed sample (0.05...0.13 g) is solved in 10 ml DMF. After dilution with water, the sample is titrated with NaOH solution in presence of ABT to blue colour appearence.

For titration in presence of aniline an another sample, in a dry beaker (thus is avoid hydrolysis), are treated with an aniline – DMF mixture (1:5, v/v). If the sample is directly solved in DMF, a subsequently addition of aniline is non-efficacious. Alow the reaction mixture to stand for 10...15 min. in a dark place in order to assure the quantitative development of reaction (6). Then dilute it with

water. Supplementary, a new quantity of precipitate has been formed. Next it is titrated with NaOH solution using ABT as indicator.

In the absence of aniline, in reactions (3),...,(5) for every mole of –COCl two moles of NaOH are consumed. In the presence of aniline only one mole of NaOH is used.

In titrations without and with aniline, the difference between hydroxide consumption to –COCl groups has been equivalent.

If we suppose that the solution of NaOH is 0.1 N, a and b being the quantities of sample titrated in the absence and in presence of aniline respectively, n_1 and n_2 – the solution volumes of hydroxide used in the two cases, the next relations are available:

$$\frac{(n_1 - n_2)0.1}{a} = \text{mmoles} - \text{COCl/g sample},$$

$$\left(\frac{2n_2}{b} - \frac{n_1}{a}\right) 0.1 = \text{mmoles} - \text{COOH/g sample}.$$

The obtained results are given in the Table 2.

Table 2

Analysis of Technical Terephthaloyl Dichloride

No.	Sample weight a, [g]	Consumed NaOH mmoles/g	Sample weight b, [g]	Consumed NaOH mmoles/g	mmoles/g sample	
	without aniline		with aniline		–COCl	–COOH
1	0.0513	18.2200	0.1005	10.8278	7.3922	3.4356
2	0.1267	18.2487	0.1000	10.8640	7.3847	3.4793
3	0.1023	18.1474	0.0581	10.9033	7.2441	3.6592
4	0.0584	18.2357	0.0753	10.6972	7.5385	3.1587
		18.2130		10.8231	7.3899	3.4332

If in titration of sample in presence of aniline the hydroxide consumption is greather than 50% with respect to those used in absence of aniline, the existence of free carboxylic groups in technical terephthaloyl dichloride has been prouved.

2.4. The Mixture of Terephthaloyl Dichloride, Terephthalic and Hydrochloride Acids Analysis

The synthetic samples by mixing technical terephthaloyl dichloride and terephthalic acid in different ratios have been prepared.

To 0.05...0.12 g of above mixtures, hydrochloride acid as standard solution has been added. A first sample of this mixture is titrated with NaOH solution. Thus the total acidity arrising in free HCl, –COOH groups and the same obtained compounds in hydrolysis of –COCl groups has been neutralized.

Another sample containing only terephthalic acid and terephthaloyl dichloride is treated with aniline – DMF mixture in previous conditions mentioned in § **2.2.** After the quantitative evolution of reaction (6) the hydrochloride acid is added in the same quantity as in the parallel sample. In titration with NaOH solution the free hydrochloride acid, –COOH groups and aniline hydrochloride are neutralized according to reactions (3), (5), (7). The difference between NaOH consumption in the two titrations is equivalent to –COCl groups.

By argentimetrically method the total content of chloride ions (HCl and –COCl) has been determined. For this reason, after the dissolution of the sample that contains the all three components in the mixture DMF – water, 2...4 ml concentrated HNO_3 and 0.5...1.0 ml saturated solution $KMnO_4$ have been added, in order to destroy the organic skeleton. The excess of $KMnO_4$ is removed using perhidrol. It is added then a well-known volume of standard $AgNO_3$ solution (15...20 ml). The unreacted $AgNO_3$ is titrated with standard NH_4SCN solution. The end-point of titration is established with ferric ammonium sulphate solution. The argentimetrically titration could be realized on the same sample resulted after the total acidity neutralization.

To calculate the content of these three components from mixture, the previous symbols used in technical terephthaloyl dichloride analysis have been preserved. In addition, if n_3 and n_4 are the volumes of $AgNO_3$ 0.1 N and NH_4SCN 0.1 N solution respectivelly, we could write:

$$\left[\frac{n_2}{b} - \frac{1}{a}(n_3 - n_4 - n_1)\right] 0.1 = \text{ mmoles HCl/g sample},$$

$$\left[\frac{n_2}{b} - \frac{1}{a}(n_3 - n_4)\right] 0.1 = \text{ mmoles } -\text{COOH/g sample}.$$

This is true only supposing that the titration is performed on the sample resulted after neutralization of the total acidity.

The content of –COCl groups is expressed using the relation previously established in § **2.2.** The obtained results are given in the Table 3.

Table 3

Analysis of the Mixture Containing Terephthaloyl Dichloride, Terephthalic and Hydrochloride Acids

No.	mmoles NaOH/g sample		mmoles/g sample			
	without aniline	with aniline	Cl total	–COCl	–COOH	HCl
1	15.7008	12.8068	5.6190	2.8940	7.1878	2.7250
2	15.8721	12.6537	6.0809	3.2184	6.5728	2.8625
3	15.8081	12.7172	5.8475	3.0909	6.8697	2.7566
	15.7937	12.7259	5.8491	3.0678	6.8768	2.7814

3. Conclusions

1. In all tested solvents we selected the mixture DMF – dioxane – water and DMF – water as best suitable solvents for dissolution of terephthaloyl dichloride as well as accomplished components in the crude product.

2. Certain acidity of dioxane imposes a suitable correction in the consumption of NaOH. Thus we prefer the mixture DMF – water (1:2, v/v).

3. The system DMF – water has an essential advantage namely, the clearly evidence of the end-point of titration.

4. The experimental conditions in the analysis of the components involved in synthesis of terephthaloyl dichloride from terephthalic acid have been established.

5. Because the above method involves an appreciable working volume and the experimental data exhibit a relative great average deviation, we proposed the application of potentiometrical technics. In this order, the obtained results will be the object of a next paper.

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ANALIZA DICLORURII DE TEREFTALOIL TEHNICE PRINTR-O METODĂ TITRIMETRICĂ

(Rezumat)

În vederea caracterizării produşilor rezultaţi la sinteza diclorurii de tereftaloil se propune stabilirea condiţiilor optime pentru solubilizarea şi determinarea cantitativă a acestora. Metoda reprezintă o adaptare şi îmbunătăţire a procedeelor generale de analiză a clorurilor acizilor carboxilici cunoscute în literatură.

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WIEDERGEWINNUNG VON VANADIUM DURCH EXTRAKTION IN SAUREM MEDIUM AUS VERBRAUCHTEN KATALYSATOREN

VON
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1. Vorwort

Das Vanadiumpentoxyd ist die wichtigste Verbindung des Vanadiums, vor allen wegen seiner vielfältigen Verwendung, z.B. in der anorganischen Industrie in den katalytischen Oxydationsprozessen von Schwefeldioxyd zu Schwefeltrioxyd, in der organischen Industrie besonders bei der Oxydierung des Nafthalins zu Phtalsäureanhydrid, des Äthanols zu Essigsäureanhydrid und Essigsäure und in der Adipinsäureindustrie. Deshalb ist sein Verbrauch sehr groß, was seine Gewinnung aus Erzen, aber auch aus wiederverwertbaren Produkten notwendig macht. Da in Rumänien keine Vorräte an Vanadiumerzen existieren, ist das Vanadiumpentoxyd ein Importartikel oder muß durch Wiederverwertung der Vanadiumerzeugnisse gewonnen werden, besonders aus verbrauchten Katalysatoren, wodurch sich sein Import wesentlich verringert.

Zur Zeit wird ein breites Spektrum von Vanadiumkatalysatoren benutzt, in dem die Hauptkomponente, das Vanadiumpentoxyd, mit 6...11% vorhanden ist [1].

Der Übergang des Katalysators vom aktiven zum inaktiven Stadium geschieht nach längerem Gebrauch, wenn das Vanadium (V) zu Vanadium (IV) desoxydiert und die aktiven Zentren auf der Oberfläche des Katalysators mit unlösbaren Verbindungen verstopft werden und somit die Übertragung des Sauerstoffs zur Reoxydierung des Vanadiums verhindert wird. Aus diesem Grunde können die verbrauchten Katalysatoren nicht mehr in den Katalyseprozessen verwendet werden.

In der Fachliteratur findet man einige Arbeiten zur Regenerierung und Wiederverwertung von verbrauchten Katalysatoren. Zum Beispiel wurde ein Verfahren zur Verwertung des Vanadiums aus verbrauchten Katalysatoren durch Extraktion mit gasförmiger Chlorwasserstoffsäure vorgeschlagen, wordurch man Vanadium in Form von Vanadium (IV)- und Vanadium (III)-oxychloriden [4] erhält oder durch Reduktion von Vanadium (V) zu Vanadium (IV) mit Formol, infolgedessen man Vanadylsulfatlösungen erhält [5], [6] die nur zur Herstellung von neuen katalytischen Stoffen verwendet werden.

In den sauren Lösungen mit einem pH-Wert kleiner als 3 existiert ein Gleichgewicht durch folgende Reaktion [3]:

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \quad (1)$$

Auf der Grundlage dieses Gleichgewichts wird die Extraktion des Vanadiums in Form von Vanadylsulfat angestrebt, da dieses im sauren Medium sehr gut löslich ist. Zur Verschiebung des Gleichgewichts zur Bildung des Vanadylions wird ein schwaches Reduktionsmittel zugesetzt, um nicht die Reduktion des Vanadiums zu einem Oxydationsstadium Kleiner als IV zu provozieren.

In dieser Arbeit werden unsere Bemühungen zur Herstellung von Vanadiumpentoxyd und Ammoniummetavanadat aus verbrauchten Katalysatoren, die bei der Umwandlung des Schwefeldioxyds zu -trioxyd verwendet werden, vorgestellt.

2. Experimenteller Teil

Zum Zwecke einer Wiederverwertung der verbrauchten Vanadiumkatalysatoren wurde die Methode der Extraktion des Vanadiums als Vanadylsulfat in Schwefelsäure angewendet. In unseren Experimenten wurde ein verbrauchter Katalysator, Typ Wolfen, mit 2,02% V_2O_4 und 2,24% V_2O_5; 2,5% Fe_2O_3; 3,92% Al_2O_3; 76,95% SiO_2 und 6,02% K_2O verwendet.

In den Laborversuchen wurde mit einem verbrauchten, fein gemahlenen Katalysator mit einer Korngröße unter 0,1 mm gearbeitet.

In einem Sulfonierkolben mit Rührer und Thermometer wurde zur Extraktion der verbrauchte Katalysator und destilliertes Wasser eingefüllt. Das optimale Verhältnis fest/flüssig wurde mit 1:5 festgelegt. Es wurde mit 400 g des verbrauchten Katalysators gearbeitet. Um der möglichen Reduktion des Vanadiums zum Oxydationsstadium (III) vorzubeugen, wurde eine halbe Stunde Luft durch die Suspension geperlt, bei einer konstanten Temperatur von 90°C. Man stellte fest, daß die Oxydation des Vanadiums (IV) zu Vanadium (V) in dieser Zeitspanne unbedeutet ist, was auch von anderen Autoren bestätigt wurde [5].

Nach der Luftdurchperlung wurde die Suspension 2,5 Stunden weiter bei 90°C gehalten. In dieser Zeit findet die Lösung eines Teils des Vanadiums als Vanadylsulfat auf der Grundlage von Schwefelsäure, gebildet aus dem Schwefeltrioxyd der Ausgangskatalysatormasse, statt. In dieser Etappe bleibt der pH-Wert wegen der Schwefelsäure bei 1,5. Zur Reduktion des Vanadiums (V) zu Vanadium (IV) und dessen Aufschließung als Vanadylsulfat wird Schwefelsäure und Oxalsäure zugegeben. Für 400 g Katalysator werden 40 ml 1:1 verdünnte Schwefelsäure und 1 g Oxalsäure als 10%-ige Lösung hinzugefügt. Folgende Reaktionen finden statt:

$$(2)\quad V_2O_5 + H_2C_2O_4 \rightarrow 2VO_2 + 2CO_2 + H_2O, \qquad (3)\quad VO_2 + H_2SO_4 \rightarrow VOSO_4 + H_2O$$

Die Schwefelsäuremenge, die hinzugefügt wird, muß im Überschuß gegenüber der stöchiometrischen Berechnung sein, damit die Extraktion quantitativ abläuft, und die Oxalsäuremenge muß stöchiometrisch sein, damit kein Überschuß an Reduktionsmittel entsteht im Hinblick auf die weitere Bearbeitung der Lösung. Nach Zugabe der Schwefel- und Oxalsäure wird die Suspension weiterhin 4 Stunden bei 90°C unter Rühren belassen, wobei sie einen pH von 0,5 hat. Durch quantitative Bestimmungen wurde festgestellt, daß die Zeit von 4 Stunden unter den obengenannten Bedingungen ausreicht, das Vanadium (V) zu Vanadium (IV) zu reduzieren und in Form von Vanadylsulfat aufschließbar zu machen. Die Bestimmung des Vanadiums wurde nach den Literaturangaben durchgeführt [12], durch Titrierung mit Mohr-Salz in Anwesenheit von Diphenylamin. In Abb. 1 wird die Kinetik der

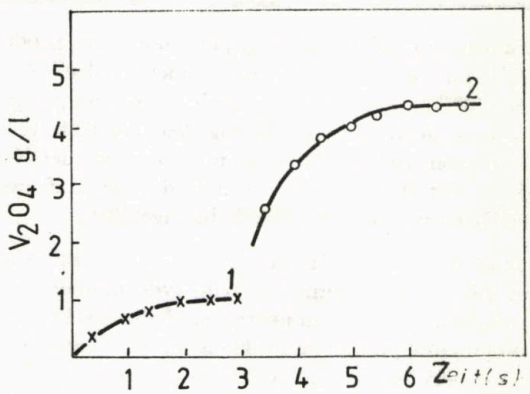

Abb. 1.– Die zeitabhängige Veränderung der Konzentration des Vanadiumtetraoxyds in flüssiger Phase: *1* – vor der Zugabe der Reaktionsmittel; *2* – nach der Zugabe der Reaktionsmittel.

Aufschließung der Vanadiumverbindungen aus der katalytischen Masse in Form von Vanadylsulfat dargestellt.

Nach siebenstündiger Extraktion wurde durch Filterung der unlösliche Teil der Vanadylsulfatlösung getrennt. In die Lösung ging ein großer Teil des Vanadiums als lösliches Vanadiumsulfat über. Im umlöslichen Teil blieb der durch Adsorption und andere Prozesse gebundene Teil zurück. Zur kompletten Extraktion des Vanadylsulfats wird dem Rest wiederum destilliertes Wasser im Verhältnis fest/flüssig von 1:5 zugefügt, auf die Temperatur von 90°C gebracht, Schwefelsäure bis zum pH=0,5 zugefügt und zwei Stunden belassen. Diese Operation wird wiederholt bis aus dem festen Bestandteil die Gesamtmenge an Vanadium extrahiert wurde. In Tabelle 1 wird der Prozentsatz von V_2O_4, der im festen Rest nach jeder Extraktion verblieben ist, wiedergegeben.

Tabelle 1

In der festen Masse Zurückgebliebene Vanadiumtetraoxydmenge nach jeder Extraktion

Extraktion	V_2O_4, [%]	V_2O_4, [%]	V_2O_4, [%]
I	2,36	2,32	2,29
II	1,07	1,11	1,12
III	0,14	0,15	0,13
IV	0,14	0,12	0,12
V	0,13	0,11	0,12

Da das Vanadium im Extrakt neben Fe (III)- und Al (III)-Verbindungen sich befindet, ist seine Trennung von diesen Verbindungen erforderlich. Dafür konnen mehrere Methoden, wie die Extraktion unter der Form von Ionenkomplexen des Vanadiums (IV) mit einingen organischen Basen in aliphatischen Alkoholen

[7], die Extraktion mit Di-2-äthylhexylphosphorsäure [8] oder die Oxydierung des Vanadium (IV) zu Vanadium (V) angewendet werden. Zu diesem Zweck wurde unter Wärme (50°C) die vanadyllösung mit Wasserstoffperoxyd oxydiert. Die Wasserstoffperoxydmenge variiert in Abhängigkeit der Katalysatorsorte und bei gleicher Sorte auch von der Schicht im Kontaktofen, wo der Katalysator herstammt. Die Behandlung mit Wasserstoffperoxyd wird durch stufenweises Zufügen bis zum wechseln der Farbe von blau in rotgelb durchgeführt.

Dann fand die weitere Trennung statt, unter Berücksichtigung der Eigenschaften der Eisen- und Aluminiumhydroxyde und der Vanadiumverbindungen beim Übergang vom sauren zum neutralen Medium [11], [12]. Diese Lösung wurde mit Ammoniumhydroxyd und im Einklang mit den Daten aus der Fachliteratur behandelt; bei pH=1,5 beginnt das Ausfällen des Eisenhydroxyds und bei pH=2 das Ausfällen des Vanadiumpentoxyds. Durch diese Methode wurde das Vanadium von den Fe (III)- und Al (III)-Verbindungen getrennt. Der Extrakt der ersten Trennung wird auf pH=2 gebracht und unter Rühren zur kompletten Ausfüllung des Vanadiumpentoxyds gekocht. Das in der Lösung enthaltene Aluminium fällt nicht aus, weil das Aluminiumhydroxyd erst bei pH=3,3 auszufällen beginnt. Die Ausfällung des Vanadiumpentoxyds ist komplett, wenn das flüssige Medium farblos bis schwach gelb geworden ist. Aus den experimentellen Daten schließt man, daß die komplette Ausfällung bei Verdampfung von ca. 2/3 der Ausgangslösungsmittelmenge stattfindet. Da während der Ausfällung des Vanadiumpentoxyds auch das Eisenhydroxyd mit ausfällt, wird der Niederschlag zur Reinigung in einer 1%-igen Natriumhydroxydlösung gelöst. Das Vanadiumpentoxyd wird komplet aufgeschlossen, während das Eisen als Niederschlag erhalten bleibt und durch Filterung getrennt werden kann. Die Natriumvanadatlösung wird mit Schwefelsäurelösung von 1 M auf pH=2 gebracht, und durch Sieden werden ca. 2/3 des Lösungsmittels entfernt, wobei das Vanadiumpentoxyd quantitativ ausfällt.

400 g Katalysator ergibt 13,30 g Vanadiumpentoxyd, was 78% der Ausgangsmenge entspricht. Aus der Natriummetavandatlösung kann auch Ammoniummetavanadat gewonnen werden. Zu diesem Zweck wird der pH-Wert der Lösung mit Schwefelsäure (1 M) auf 7 gebracht, dann führt man die Ausfällung mit einem gesättigten Ammoniumchlorid im Überschuß gegenüber der stöchiometrischen Menge durch. Aus derselben Katalysatormenge erhielt man 24,35 g Ammoniummetavanadat, was 80% darstellt.

Die Prozesse, die während der Extraktion stattfanden, wurden auch durch die Bestimmung der Leitfähigkeit der entsprechenden Lösungen untersucht, wobei ein Konductometer vom Typ OKM 102 verwendet wurde. Die Proben dafür wurden halbstündlich aus der Ausgangssuspension entnommen, sowohl vor der Reduktion mit Oxalsaure als auch nach der Reduktion des Vanadiums (V) zu Vanadium (IV).

Die Leitfähigkeit wurde nach der Trennung der festen Phase des Vanadylsulfats durch Filterung und Verdünnung im Verhältnis von 1:100 mit destilliertem Wasser gemessen. Die Kurve der Löslichheitsänderung ist im Abb. 2 dargestellt.

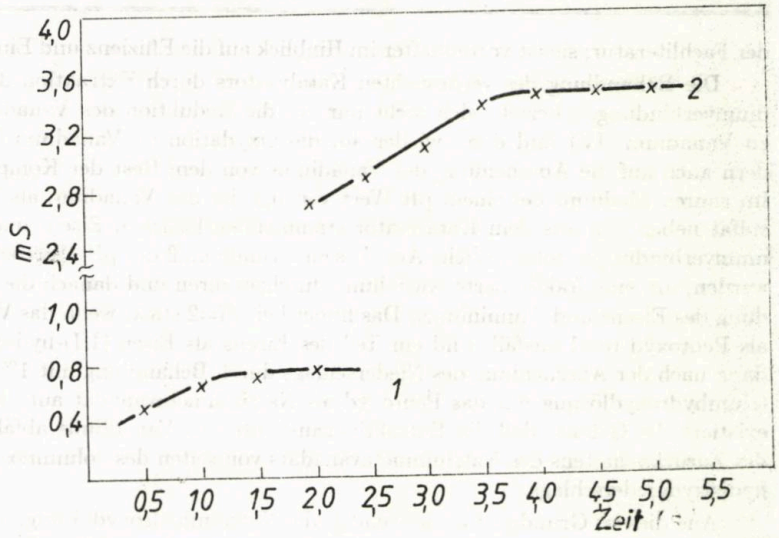

Abb. 2.– Die zeitmäßige Veränderung der elektrischen Leitfähigkeit der Vanadylsulfatlösung: *1* – vor der Zugabe der Reaktionsmittel; *2* – nach der Zugabe der Reaktionsmittel, von Schwefel- und Oxalsäure.

3. Interpretation der Ergebnisse

Aus den Fachliteraturdaten [11], [12] sowie aus eigenen experimentellen Daten folgt, daß die Wiedergewinnung des Vanadiums aus verbrauchten Katalysatoren vorteilhafter ist, wenn das Vanadium in nur einem Oxydationszustand vorliegt, (IV) oder (V). In dieser Arbeit wurde die Extraktion der Vanadiumverbindungen durch Reduktion in saurem Medium zu Vanadium (IV) und dann ihre Oxydation zu Vanadium (V) vorgestellt. Aus den experimentellen Daten folgt, daß nach der Reduktion die gesamte Menge an Vanadium in der Form von löslichem Vanadylsulfat vorliegt. Die Trennung des unlöslichen Teils des Katalysators kann nicht mit einer Ausbeute von 100% durchgeführt werden, weil das Vanadium teilweise von der festen Masse zurückbehalten wird. Aus diesem Grunde wurden die Extraktionen solange wiederholt, bis praktisch kein Vanadium mehr extrahiert werden konnte, d.h. nach der dritten Extraktion blieb die von der festen Masse zurückbehaltene Vanadiummenge fast konstant, was 6...7% Vanadiums in der Ausgangsmasse darstellte. Da die Vanadium (IV)-verbindungen weniger verwendet werden, mußte nach der Extraktion die Gesamtmenge von Vanadium (IV) zu Vanadium (V) oxidiert werden. Dazu kommt die Tatsache, daß die Verbindungen des Vanadium (V) leichter zu trennen sind. In der Fachliteratur wird die Trennung der Vanadiumverbindungen durch Extraktion mit aliphatischen Alkoholen, Ionenaustauschern usw. angegeben [9], [10]. Die von uns angewendete Abscheidungsmethode für die Vanadiumverbindungen aus verbrauchten Katalysatoren unterscheidet sich von denen

der Fachliteratur; sie ist vorteilhafter im Hinblick auf die Effizienz und Einfachheit.

Die Behandlung des verbrauchten Katalysators durch Extraktion der Vanadiumverbindungen bezieht sich nicht nur auf die Reduktion des Vanadiums (V) zu Vanadium (IV) und dann wieder auf die Oxydation zu Vanadium (V), sondern auch auf die Abscheidung des Vanadiums von dem Rest der Komponenten. Im sauren Medium, bei einem pH-Wert von 0,5, ist das Vanadium als Vanadylsulfat neben den aus dem Katalysator stammenden löslichen Eisen- und Aluminiumverbindungen total löslich. Aus diesem Grunde muß der pH-Wert angehoben werden, um eine fraktionierte Ausfällung durchzuführen und danach die Abscheidung des Eisens und Aluminiums. Das findet bei pH=2 statt, wenn das Vanadium als Pentoxyd total ausfällt und ein Teil des Eisens als Eisen (III)-hydroxyd, um dann nach der Abscheidung des Niederschlags durch Behandlung mit 1%-iger Natriumhydroxydlösung nur das Pentoxyd als Natriummetavanadat aufzulösen. Es existiert die Gefahr, daß die Extraktionsausbeute des Vanadiums abfällt wegen des Zurückbehaltens des Natriummetavanadats von seiten des voluminösen Eisenhydroxydniederschlags.

Aus diesem Grunde ist es notwendig, die Natriumhydroxydlösung, in der das Vanadiumpentoxyd aufgeschlossen wird, sehr stark zu rühren. Gleichfalls muß der Niederschlag, der eventuell noch lösliches Natriummetavanadat beihalten könnte, mit Natriumhydroxydlösung gespült werden.

Die Verfolgung der Aufschließung des Vanadiums in Form von Vanadylsulfat aus der Masse des behandelten Katalysators erwies sich als wirksam durch die Bestimmung der elektrischen Leitfähigkeit der Extrakte, so wie es im experimentellen Teil beschrieben wurde. Man stellt fest, daß vor der Reduktion, während der Aufschließung des Vanadiums, die elektrische Leitfähigkeit in 2,5 Stunden ansteigt, danach das Anwachsen unbedeutend ist und asymptotisch gegen einen konstanten Wert strebt. Nach Zugabe von Schwefel- und Oxalsäure wächst die Luftfähigkeit der Lösung, während die Reduktion stattfindet, wiederum gegen einen konstanten Wert (Abb. 2, Kurve *2*). Das unbedeutende Anwachsen der Leitfähigkeit beobachtet man nach 3,5...4 Stunden. Aus den experimentellen Bestimmungen folgt die volle Übereinstimmung zwischen den chemischen Bestimmungsmethoden des extrahierten und nicht extrahierten Vanadiumbestandteils und den elektrischen Leitfähigkeiten derselben, chemisch analysierten Proben.

4. Schlußfolgerungen

Man stellt eine Modalität zur Wiedergewinnung der aktiven Komponente des Vanadiumpentoxyds, aus vebrauchten Katalysatoren vor. Dies wurde in unterschiedlichen Etappen durchgeführt und zwar durch Abscheidung der Vanadiumverbindungen bei verschiedenen pH-Werten.

Die Methode der Wiedergewinnung von Vanadium aus vebrauchten Katalysatoren, obwohl unter Laborbedingungen getestet, kann auf Pilotanlagen oder industriemäßig angewendet werden zur Wiederverwertung der Vanadiumverbindungen,

die in der Oxydationskatalyse des Schwefeldyoxyds zu Schwefeltrioxyd verwendet werden.

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Technische Universität „Gh. Asachi", Jassy, Lehrstuhl für anorganische Chemie

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RECUPERAREA VANADIULUI, PRIN EXTRACŢIE ÎN MEDIU ACID, DIN CATALIZATORI UZAŢI

(Rezumat)

Se prezintă un mod de valorificare a catalizatorilor uzaţi de vanadiu folosiţi în cataliza de oxidare a dioxidului de sulf la trioxid de sulf.

Extracţia vanadiului se realizează sub forma de soluţie de sulfat de vanadil, în mediu de acid sulfuric, folosind ca reducător al vanadiului (V) la vanadiu (IV), acidul oxalic. Soluţia de sulfat de vanadil este supusă oxidării cu apă oxigenată şi apoi prelucrată în vederea obţinerii pentaoxidului de vanadiu.

Determinările experimentale s-au efectuat folosind: analiza chimică, metoda conductometrică şi cea pH-metrică.

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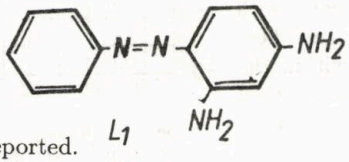
STUDY ON REACTIONS OF $K_2[PdCl_4]$ WITH SOME AZO DYES

BY
N. FOCA

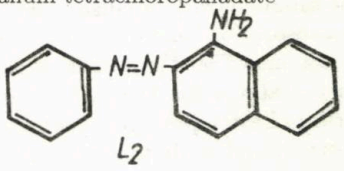
1. Introduction

The palladium (II) can react as $K_2[PdCl_4]$ complex in neutral or slighty acid medium, with some azo dyes, containing both azo group as well as other functional group in α position, namelly –OH or $-NH_2$ [1],...,[4].

In the present paper, the results obtained by the study of 2,4-diaminoazobenzene (L_1), azo-α-naphtylamine (L_2) and kalium tetrachloropalladate



L_1



L_2

are reported.

2. Experimental

The $K_2[PdCl_4]$ was taken in our study as a solution with the DMF – H_2O solvent mixture, 85% DMF – 15% H_2O [5].

The $K_2[PdCl_4]$ solution thus prepared, of initial concentration between $0.5\times$ $\times 10^{-2}$ ... 1×10^{-2} moles l^{-1}, are stable for a rather time. By diluting them with dimethylformamide (DMF) the solution of desired concentrations have been prepared.

With the working concentrations $K_2[PdCl_4]$ does not show absorption bands within visible region.

The 2,4-diaminoazobenzene and azo-α-naphtylamine have been used as solutions in ethyl alcohol p.a. since these dyes are not soluble in water.

Since the pH value of the reaction medium is particularly important the experiments have been carried out with DMF, ethylalcohol p.a. or DMF ethylalcohol mixture.

The solvents had to be chosen properly for a pH value of about 7 since both 2,4-diaminobenzene (crysoidine, L_1) and benzen-azo-α-naphtylamine (L_2) behave as indicators in acid medium.

The first dye (L_1) has a transition interval within pH=4...6 turning its orange colour into yellow. The latter dye changes its colour from yellow, in aqueous medium, or brown-yellow in ethanol to violet-red in acid medium (pH=0...5.5) [6].

3. Results and Discussion

3.1. Electronic Absorption Spectra

The reaction between crysoidine [4] and benzene azo-α-naphtylamine (L_2) has been studied based on the UV electronic absorption spectra.

The UV electronic spectra have been recorded for the two ligands, L_1 and L_2, under different combination ratios of Pd(II) – L_1 and Pd(II) – L_2.

The kalium tetrachlorpalladite in aqueous solution shows an absorption band within the visible region with λ_{max} = 430 nm (Fig. 1). In these cases the modifications in the absorption electronic spectra within the visible range have especially been followed since they are important and easily to analyse (Figs. 2 and 3).

The analyses of the electronic spectra for the $K_2[PdCl_4]$ – L_1 system are illustred by the data in Table 1 and those for the $K_2[PdCl_4]$ – L_2 system, in Table 2.

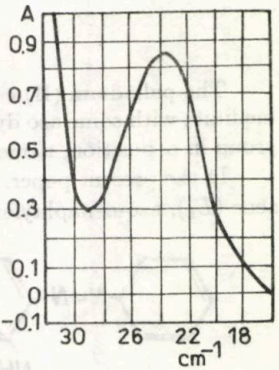


Fig. 1.– Absorption electronic spectrum of $K_2[PdCl_4]$ in aqueous solution; $C = 1 \times 10^{-3}$ mol^{-1}; layer thickness – 1 cm.

3.2. Determination of Metal – Ligand Combination Ratios for the $K_2[PdCl_4]$ – 2,4-diaminoazobenzene (L_1) System

The composition of the complexes formed in the $K_2[PdCl_4]$ – L_1 system was determined spectrophotometrically by means of the molar ratios method (applied in two variants maintaining in the sample series: a) either C_M = const.; b) either C_L = const.), the J o b method and others.

3.3. Molar Ratio Method [9]

The data obtained by this method, with $C_{K_2[PdCl_4]}$ = const. = 1×10^{-4} moles l^{-1}, are depicted in Fig. 4. These data are indicative of two complexes occurring by the reaction between $K_2[PdCl_4]$ and L_1 since the obtained stright lines show

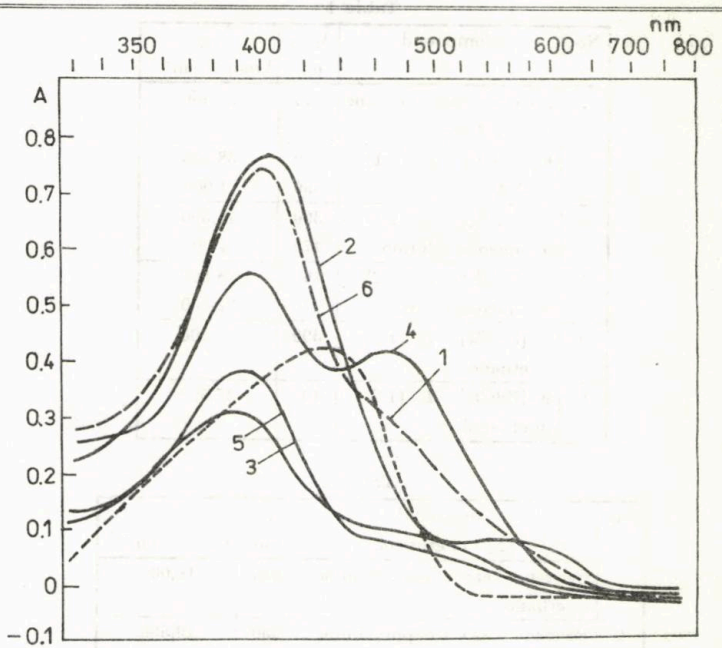


Fig. 2.– Absorption electronic spectra within 350 ... 750 nm for L_1 and for different metal – ligand ratios: *1* – 2.4-diaminoazobenzene (L_1) in DMF; *2* – $K_2[PdCl_4]+L_1$ (1:1) in DMF; *3* – $K_2[PdCl_4]+L_1$ (1:2) in DMF; *4* – $K_2[PdCl_4]+L_1$ in aqueous solution; *5* – $K_2[PdCl_4]+L_1$ (1:1) in ethanol; *6* – $K_2[PdCl_4]+L_1$ (1:2) in ethanol; V_{final} = 10 cm^3; cell layer thickness – 0.2 cm.

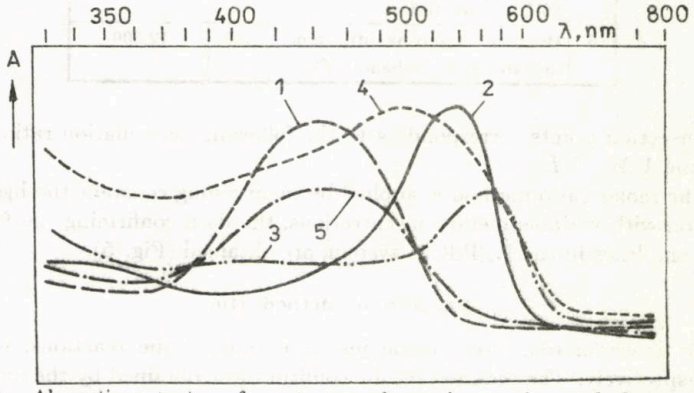


Fig. 3.– Absorption spectra of reactants and reaction products of the system $K_2[PdCl_4]$ – benzene-α-naphtylamine (L_2); *1* – Benzene – azo-α-naphtylamine in ethanol (L_2); *2* – Benzene – azo-α-naphtylamine in HCl (1:1); *3* – $L_2+K_2[PdCl_4]$ (1:1) in ethanol 90% – water 10%; *4* – $L_2+K_2[PdCl_4]$ (2:1) in ethanol 90% – H_2O 10%; *5* – Benzene – azo-α-naphtylamine in water 90% – ethanol 10%; V_{final} = 10 cm^3; layer thicknes – 0.2 cm.

Table 1

No.	Compound	λ_{max} nm	ε_{max} $l.mol^{-1}.cm^{-1}$
1	2,4-Diaminoazobenzene (L_1) in DMF	440	21,500
2	$K_2[PdCl_4]$ – L_1 (1:1) in DMF	410 580	38,500 4,000
3	$K_2[PdCl_4]$ – L_1 (1:1) in aqueous solution	390 470	15,500 4,000
4	$K_2[PdCl_4]$ – L_1 (1:2) in aqueous solution	400 470	28,000 22,000
5	$K_2[PdCl_4]$ – L_1 (1:1) in ethanol	390	19,500
6	$K_2[PdCl_4]$ – L_2 (1:2) in ethanol	405	37,500

Table 2

No.	Compound (L_2) in ethanol	λ_{max} nm	ε_{max} $l.mol^{-1}.cm^{-1}$
1	Benzene – azo-α-naphtylamine in ethanol	440	18,000
2	Benzene – azo-α-naphtylamine in HCl (1:1)	530	19,500
3	L_2 – $K_2[PdCl_4]$ (1:1) in ethanol 90% – water 10%	405 570	6,000 12,000
4	L_2 – $K_2[PdCl_4]$ (2:1) in ethanol 90% – water 10%	505	19,500
5	Benzene – azo-α-naphtylamine in water 90% – ethanol 10%	440	12,500

two intersection points corresponding to the following combination ratios: 1 M : : 1 L_1 and 1 M : 2 L_2.

If the molar ratio method is applied by maintaining constant the ligand concentration with variable metal concentrations, the data confirming the formation of two complexes in the $K_2[PdCl_4]$ system, are obtained (Fig. 5).

3.4. J o b Method [10]

The determinations were made just after mixing the reactions, 6 and 12 hours respectively. The required results confirm those obtained by the molar ratio method, regarding the formation of two complex ions (Figs. 6 *a* and 6 *b*).

The fact deserves mention that the formation of the two complexes is deduced from the same determination series (J o b) making the required corrections, namely eliminating the absorbance of the ligand excess at $\lambda_{max} = 470$ nm, as can be seen

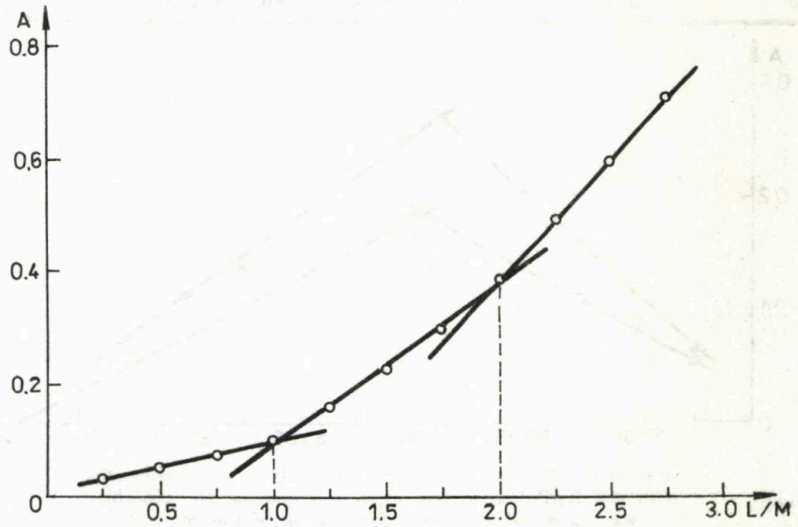


Fig. 4.– Results obtained by the study on the composition of $K_2[PdCl_4]$ – L_1 system by the mole ratio method; $C_{K_2[PdCl_4]}$=const.=1×10^{-4} mole l^{-1}, C_{L_1}=variable; V_{final} = 10 cm^3; cell = 0.2 cm.

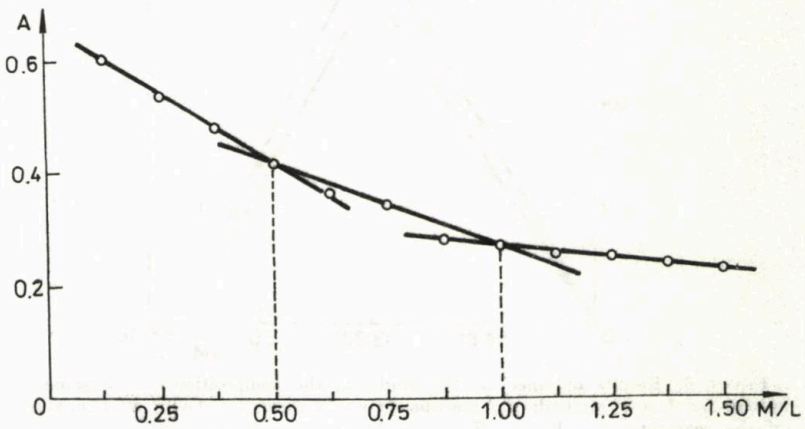


Fig. 5.– Data obtained by titration of a constant ligand amount with variable metal amounts; V = 10 cm^3; $C_L = 1 \times 10^{-4}$ mol.l^{-1}; cell = 0.2 cm.

in Fig. 7.

By applying the same method in sholying the composition of the $K_2[PdCl_4]$ – benzene azo-α-naphthylamine (L_2) system the conclusion was drawn that only

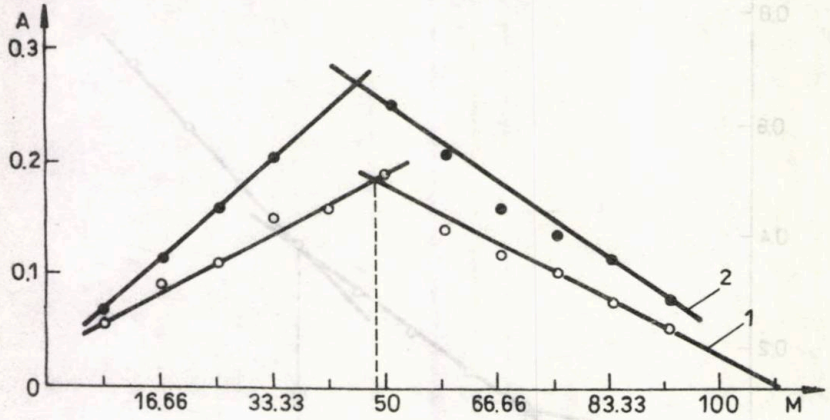


Fig. 6 *a*. Results obtained by the study of the composition with the $K_2[PdCl_4]$ system by J o b method; the absorbance was measured one hour after mixing of the reactants.

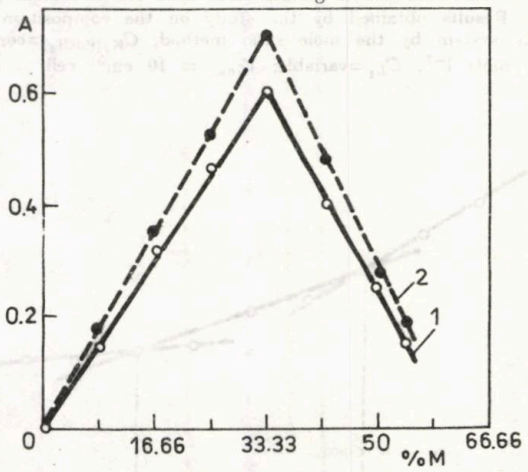


Fig. 6 *b*. Results obtained by the study on the composition of the same system by J o b method; the absorbance was measured 6 hours after mixing of the reactants; *1* – V_{final} – 7.5 cm^3; *2* – V_{final} – 10 cm^3; cell = 0.2 cm.

one complex occurs, namely, that of the $L : M$=1:1 ratio (Fig. 8).

The same results were obtained by reading the absorbance after 24 and 48 hours.

The J o b method [10] applied in the study of the $K_2[PdCl_4]$ – L_2 system confirms the combination ratio $M : L = 1 : 1$.

It was worked with two different concentrations, namely $V_1 = 5$ cm^3 and $V_2 = 10$ cm^3, the initial concentrations of the ligand and of the metal being $C_M =$

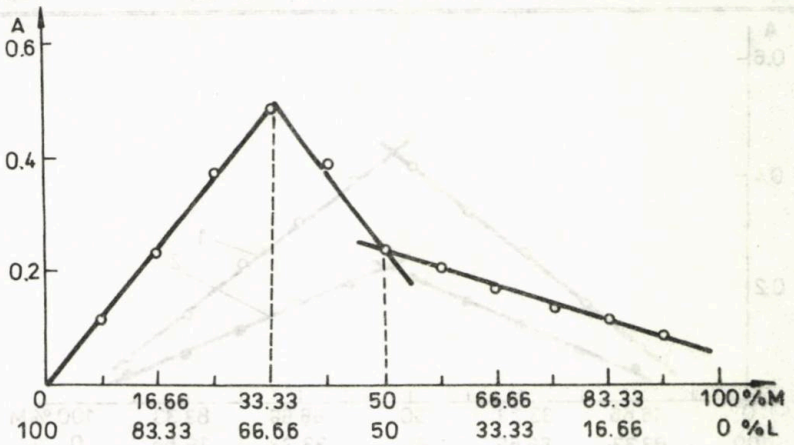


Fig. 7.– Determination of $M : L$ combination ratio for the $K_2[PdCl_4] - L_1$ system; obtained with corrected absorbance; V_{final} – 10 cm^3; cell – 0.2 cm.

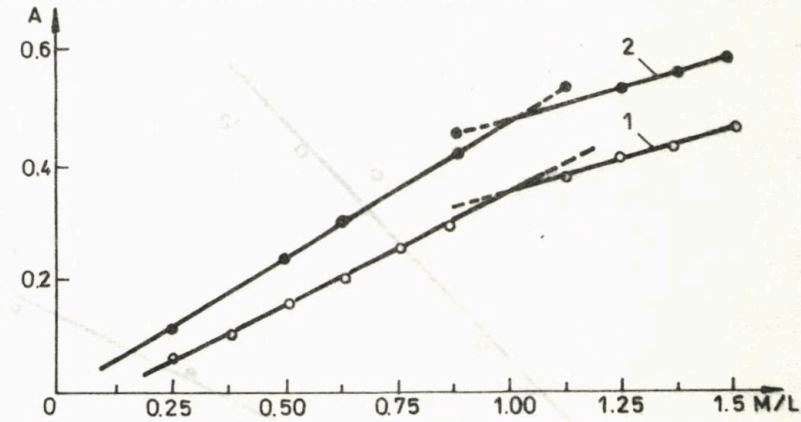


Fig. 8.– Data obtained by the study of the $K_2[PdCl_4] - L_2$ system with the molar ratio method: *1* – absorbances of solutions read after 24 hours; *2* – absorbances of solutions read after 48 hours; $V_{final} = 10$ cm^3; layer thickness – 0.2 cm.

$= C_L = 1 \times 10^{-3}$ moles l^{-1}.

The absorbance were read on stabilized solutions. The obtained results are depicted in Fig.9, where two combination ratio can be easily settled ($M : L = 1 : 1$).

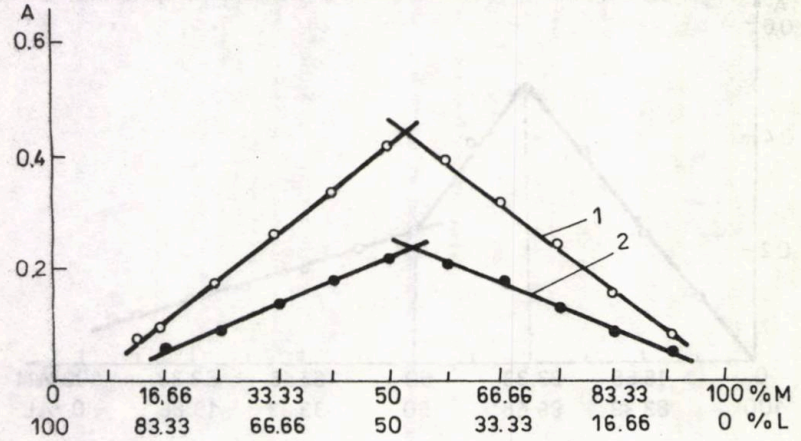


Fig. 9.– Straight lines obtained by the study on the complex composition in $K_2[PdCl_4]$ – benzene-azo-α-naphtylamine system by the continuous variation method.

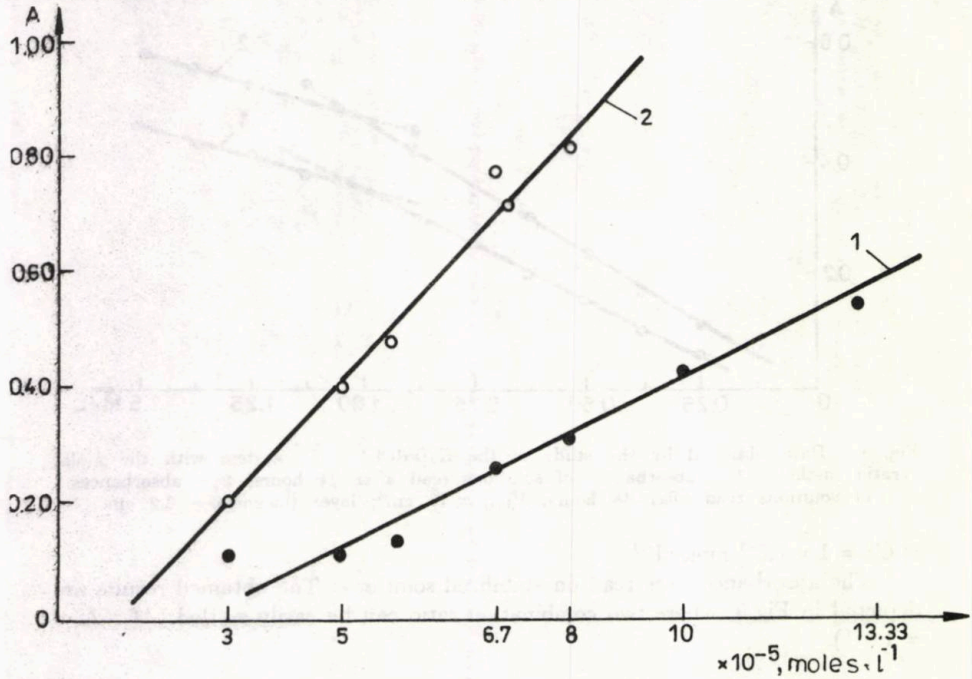


Fig. 10.– Verification of L a m b e r t - B e e r law for the complexes resulting by the reaction between $K_2[PdCl_4]$ – L_1 and $K_2[PdCl_4]$ – L_2: *1* – straight line obtained for the 1 M : 1 L_1 complex; solvent ethyl alcohol; layer thickness – 0.2 cm; *2* – straight line obtained for the 1 M : 1 L_2 complex; *3* – straight line obtained for the 1 M : 2 L_2 complex; solvent – water; cell – 0.2 cm; λ = 470 nm.

4. Verification of L a m b e r t – B e e r Law

The reaction between $K_2[PdCl_4]$ and 2,4-diaminoazobenzene (L_1) in the C_2H_5OH – DMF solvent mixture was studied.

Three new complexes are made evident, that is two in the $K_2[PdCl_4]$ – L_1 reaction and one for the $K_2[PdCl_4]$ – L_2 system. As ilustrated by Fig. 10 all the complexes resulting in the systems under study obey the L a m b e r t - B e e r law.

4.1. Stability of the Complexes in the $K_2[PdCl_4]$ – L_1 and $K_2[PdCl_4]$ – L_2 Systems

The stability constants for the 1 M : 1 L_1, 2 M : 1 L_1 and 1 M : 1 L_2 complex have been calculated.

The stability constants for the complexes of the 1 M : 1 L ratio were determined in both cases by the T u r n e r - A n d e r s o n method, and for the 1 M : : 2 L_1 complex by the E d m o n d s - B i r n b a u m method [12]. The formation constant were also calculated by the H a r v e y - M a n n i n g method [13].

The calculated values using the above mentioned methods are close to each other average being:

$$K_1(1M : 1L_1) = 3.56 \times 10^9 \text{ l.moles}^{-1};\ K_2(1M : 2L_1) = 4.64 \times 10^{12}\ l^2.\text{moles}^{-2};$$

$$K(1M : 1L_2) = 2.80 \times 10^{10}\ l^{-1}.\text{moles}^{-1}.$$

The values of the formation constants are rather big. This reflects very well the tendency of Pd(II) to form very stable complex combinations with azo dyes.

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STUDIUL REACŢIEI DINTRE $K_2[PdCl_4]$ ŞI UNII COLORANŢI AZOICI

(Rezumat)

Se prezintă rezultatele obţinute în studiul spectrofotometric al reacţiilor dintre $K_2[PdCl_4]$ cu 2,4 diaminoazobenzen şi benzen-azo-α-naftilamină. Au fost stabilite condiţiile optime de lucru, s-au determinat rapoartele de combinare $M : L_1$, cât şi $M : L_2$. De asemenea, s-au calculat constantele de stabilitate ale complecşilor din sistemele studiate.

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VERWERTUNG DES VERBRAUCHTEN NICKEL-KATALYSATORS AUS DER SPEISEÖLHÄRTUNG

VON
I. ROŞCA, DANIEL SUTIMAN, N. FOCA und AL. CONSTANTINESCU

1. Vorwort

In der Industrie wird zur Herstellung von Margarine die Speiseölhärtung bei 200°C und 2 atm. angewandt. Bei diesem Verfahren wird ein importierter Katalysator auf Nickelbasis verwendet [1], [6]. Es handelt sich um ein diskontinuierliches Verfahren und nach ungefähr 15 Herstellungszyklen wird der Katalysator inaktiv und somit unbrauchbar.

Diese Arbeit stellt einige Modalitäten einer Verwertung dieses Katalysators vor, was in zahlreichen Versuchen bis jetzt hier im Land nicht von Erfolg war. In den Ölfabriken findet man große Mengen von verbrauchtem Katalisator, z.B. in der Ölfabrik, Jassy, ca. 300 t.

Die Verwertung dieses verbrauchten Katalysators wurde in zwei Richtungen verfolgt: a) Regenerierung des Katalysators; b) Wiedergewinnung des Nickels in Form von Verbindungen mit industrieller Anwendung.

2. Experimenteller Teil

In der ersten Phase wurde die Zusammensetzung des frischen und verbrauchten Nickelkatalysators bestimmt. In einem Rührgefäß wurden bei 60°C 100 g des unverbrauchten Katalysators mit 20%-igem reinem Chlorwasserstoff im Überschüß behandelt. Nach einer halben Stunde wurde das Rühren unterbrochen und das Gefäß zum Abkühlen abgestellt. Im kalten Zustand haben sich drei Schichten abgesondert: a) eine feste Schicht, im unteren Teil, in dem SiO_2 überwiegt; b) eine flüssige Schicht – eine $NiCl_2$-Lösung; c) eine obere Schicht – ein festes organisches Produkt.

Aus dem Schmelzpunkt und der Elementaranalyse wurde gefolgert daß die feste obere Schicht aus Paraffin besteht. Durch gravimetrische Bestimmung des Nickels mit Dimethylglyosim wurde die Lösungskonzentration von $NiCl_2$ und der anderen

Komponenten abgeleitet. Der unverbrauchte Katalysator besteht aus: 20% Ni, 20% SiO_2 und 60% Paraffin.

Dann wurde auf dieselbe Weise mit mehreren Proben die Zusammensetzung des verbrauchten Katalysators bestimmt. Er enthält: 8...10% Ni, 8...10% SiO, 80...84% organische Härtungsprodukte.

2.1. Regenerierung des Katalysators

In der Fachliteratur sind zwei Modalitäten der Regenerierung von Nickelkatalysatoren bekannt, aber diese Methoden haben eine niedrige Ausbeute in der Nickelverwertung [2]. Die Regenerierung des Katalysators wurde folgendermaßen durchgeführt. In einen Sexhlet-Extrakter wurden 100 g verbrauchter Katalysator aus der Ölfabrik, Jassy, gefüllt. Zur Extraktion der organischen Verbindungen wurden mehrere Lösungsmittel verwendet nämlich: Extraktionsbenzin, Chloroform, Azeton, Petroläther und Methanol [3], [4]. In Abb. 1 ist die Veränderung der Nickelkonzentration in der festen Masse in Abhängigkeit von der Zeit, für die oben erwähnten Lösungsmittel dargestellt. Der Extraktionskolben wird von einem Heizmantel umschlossen und der Kühler wird mit einer Kühlwasserquelle gekoppelt. Der verbrauchte Katalysator wird in einen Zylinder mit Filtertuch, Typ „Petrol", der fest verschlossen ist, um einen Nickelverlust zu vermeiden, gefüllt. Die Erwärmung wird in Abhängigheit vom Lösungsmittel geführt, um ein optimale Rückflußmenge zu erhalten. Die Extraktion wird als beendet betrachtet, wenn das sifonierende Lösungsmittel ganz klar und farblos ist.

Nach der Extraktion wird der verbrauchte Katalysator, der 35...45% Nickel enthält, zur totalen Beseitigung der Fette mehrere Male unter Rühren und Wärme mit einer 10, 5 und 1%-igen Natriumhydroxydlösung im Verhältnis 1:5 (fest:flüssig) gewaschen, danach in Paraffin eingeschlossen und pastilliert. Nach entsprechenden Testen wurde festgestellt, daß die Aktivität des regenerierten Katalysators unter dem Niveau des frischen Katalysators liegt. Diese bis jetzt von uns angewandte Methode führt also nicht zu einer zufriedenstellenden Regenerierung des Katalysators.

2.2. Wiedergewinnung des Nickels

Die Herstellung von Nickelverbindungen wird zur Zeit nach klassischen Methoden durchgeführt und zwar ihre Verdrängung aus Salzen mit Säuren, entsprechend den herzustellenden Substanzen [4], [5], [7], [8]. Die als Grundstoffe verwendeten Nickelverbindungen werden importiert. Zur Ausscheidung der organischen Verbindungen aus dem verbrauchten Katalysator wurde dieselbe Methode wie in §**2.1** angewendet. Aus der Analyse der kinetischen Kurven in Abb. 1 wurde als Lösungsmittel Chloroform gewählt das im Vergleich zu den anderen Lösungsmittel eine größere Extraktionsgeschwindigkeit aufweist, und es ist nicht brennbar und billiger [3], [9].

Nach der Extraktion enthält der verbrauchte Katalysator 40...44% Nickel. Aus 100 g Katalysator erhielt man 38,3 g eines Gemisches aus Nickel und Trägersub-

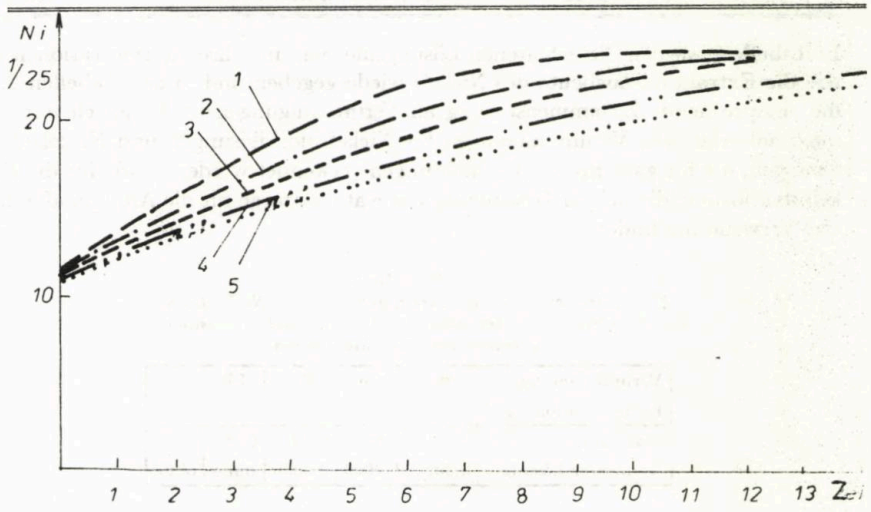

Abb. 1.– Die Veränderung der Nickelkonzentration in der festen Masse in Abhängigkeit von der Zeit fur verschiedene Lösungsmittel; *1* – Chloroform; *2* – Extraktionsbenzin; *3* – Äthyläther; *4* – Methylalkohol; *5* – Azeton.

stanz mit einem Gehalt von 43,6% Nickel. Das Gemisch Nickel/Träger wurde bear beitet im Hinblick auf die Gewinnung von Nickelchlorid- und Nickelsulfatlösunge für galvanische Beschichtung und zur Gewinnung von mit 6 Wassermolekülen kris tallisiertem festem Nickelazotat.

In einem Rührgefäß wurde der verbrauchte Katalysator bei 50°C nach de Extraktion mit entsprechenden Säuren in stöchiometrischen Mengen behandelt Die Reaktionszeit betrug 30 Min. Die Suspension wird unter Vakuum durch eine Büchnertrichter mit gewöhnlichem Papier gefiltert. Zur totalen Extraktion wird de Träger dreimal mit destillerten Wasser im Verhältnis 1:2 (fest:flüssig) behandelt.

Tabelle 1

Lösungsmengen, Lösungkonzentration und Extraktionsausbeuten an Nickel aus 100 g verbrauchten Katalysator

Lösung	Menge ml	Konzentration g/l	Ni %
$NiCl_2$	300	123,6	94,4
$NiSO_4$	295	142,7	96,3
$Ni(NO_3)_2$	300	170,7	91,2

Um Nickelchloridlösung zu gewinnen, verwendet man 60 ml 30%-ige Chlorwa serstoffsäure und für die Gewinnung von Nickelsulfatlösung werden 55 ml 40%-ig Schwefelsäure verwendet und für Nickelnitratlösung 60 ml 50%-ige Salpetersäur

In Tabelle 1 werden die erhaltenen Lösungsmengen und ihre Konzentrationen sowie die Extraktionsausbeute des Nickels wiedergegeben und in den Tabellen 2...4 die entsprechende Zusammensetzung an Verunreinigungen im Vergleich mit den maximal erlaubten Verunreinigungen für Nickelchloridlösungen und Nickelsulfatlösungen, die für galvanische Beschichtungen verwendet werden, sowie für die Nickelnitratlösung, die bei der Gewinnung von Katalysatoren für die Ammoniakindustrie Verwendung findet.

Tabelle 2

Konzentration der Verunreinigungen der $NiCl_2$-Lösung im Vergleich mit der industriell verwendeten Lösung bei galvanischen Beschichtungen

Verunreinigungen Konzentration, [g/l]	Fe	Cu	Zn	Pb	Cr
Maximum	0,1	0,02	0,03	0,002	0,01
In unserer Lösung	0,0023	0,0009	0,0036	ohne	ohne

Tabelle 3

Konzentration der Verunreinigungen der $NiSO_4$-Lösung im Vergleich mit der industriell verwendeten Lösung bei galvanischen Beschichtungen

Verunreinigungen Konzentration, [%]	Zn	Fe	Cu	Pb	Mn	Cl^-	As
Maximum	0,02	0,02	0,02	0,02	0,05	0,05	0,01
In Lösung	0,008	0,0075	0,006	0,003	–	–	–

Tabelle 4

Konzentration der Verunreinigungen des Nickelnitrats im Vergleich mit dem Nickelnitrat, das bei der Herstellung des Katalysators für die Ammoniakgewinnung Verwendet wird

Verunreinigungen Konzentration, [%]	CuO+MgO	Na_2O+K_2O	Halogene
Maximum	0,01	0,025	–
In Lösung	0,0003	0,0032	–

Aus der Nickelchloridlösung wurde durch die Behandlung mit Ammoniumkarbonat Nickelkarbonat ausgefällt, das einer Kalzinierung zur Gewinnung von Nickeloxyd unterworfen wurde. Aus 100 ml Nickelchloridlösung mit einem gehalt von 116 g/l erhielt man nach der Kalzinierung 5,3 g Nickeloxyd, was einer Extraktionsendausbeute des Nickels von 93% entspricht. Ebenfalls kann man aus den Nickelchlorid- und Nickelsulfatlösungen metallisches Nickel durch Reduktion mit Wasserstoff oder anderen Reduktionsmitteln gewinnen [4], [5], [8].

3. Schlußfolgerungen

1. Aufgrund der Experimente wurde festgestellt, daß für die Extraktion der organischen Verbindungen Lösungsmittel der laufenden Produktion, besonders Chloroform und Extraktionsbenzin, bei einer Extraktionsdauer von 5...7 Stunden verwendet werden können.

2. Die Regenerierung des Katalysators nach der von uns vorgeschlagenen Methode erwies sich als unvollständig.

3. Die Wiedergewinnung des Nickels in Form von Chlorid oder Sulfat betrachten wir als besonders vorteilhaft, da bereits eine Herstellungstechnologie für Nickelchlorid erarbeitet wurde, die in der Galvanikabteilung des TEROM, Jassy, Anwendung finden wird. Die im Labor gewonnenen Lösungen wurden im TEROM, Jassy, getestet und entsprechen der Landesnorm STAS 6705/1981.

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VALORIFICAREA CATALIZATORULUI DE NICHEL UZAT DE LA HIDROGENAREA ULEIULUI COMESTIBIL

(Rezumat)

Se prezintă două modalităţi de valorificare a catalizatorului de nichel uzat, utilizat în industrie la hidrogenarea uleiului comestibil:

I. *Regenerarea catalizatorului.* S-a efectuat prin extracţia compuşilor organici cu diverşi solvenţi, spălarea urmelor de compuşi organici cu soluţii diluate de hidroxid de sodiu, învelirea în parafină şi pastilare. Din datele experimentale de activitate catalitică a rezultat că metoda utilizată nu este avantajoasă deoarece activitatea catalizatorului regenerat nu a atins o valoare care să poată justifica reutilizarea lui.

II. *Valorificarea sub formă de compuşi utili.* S-a efectuat sub formă de soluţii de clorură de nichel, sulfat de nichel, azotat de nichel, prin tratarea catalizatorului, separat de substanţe organice, cu acizii corespunzători. Soluţiile de clorură de nichel şi sulfat de nichel s-au experimentat la staţia de acoperiri galvanice a TEROM S.A., Iaşi şi corespund STAS 6705/1981. Soluţia de azotat de nichel poate fi utilizată, din analiza impurităţilor, la fabricarea catalizatorilor din industria amoniacului.

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VAPOUR – LIQUID EQUILIBRIA OF ACETONE – ETHYLACETATE MIXTURES

BY

GH. IONESCU, D. HRIŢCU and N. AELENEI

1. Introduction

Experimental data on vapour – liquid equilibrium, obtained either in isobaric or in isothermal conditions, represent basic elements in the thermodynamic characterization of solutions. Their obtainement required – and still does – designing and improvement of adequate equipments [1],...,[8]. Also, improved methods and techniques are being developed for the analysis of phase composition [9]. The criteria involved in checking the thermodynamic consistency of experimental data are detailed [10],...,[12], as having a special significance in the design and optimization of industrial processes; thus mention will be made have, exclusively, of their involvment in the most widely applied operation in both chemistry and petrochemistry, namely fractional distillation.

The acetone–ethylacetate binary solution is largely utilised in antibiotic industries. Solvent recovery, through fractional distillation, assumes knowledge of vapour – liquid equilibrium data.

In this paper, the vapour – liquid equilibrium data, characteristic to the above mentioned solution, obtained in isobaric conditions on a G i l l e s p i e type device [13], designed by the authors, is studied. The obtained performance, of average value, meet the requirements of usual designing calculations.

2. Experimental

2.1. Materials, Apparatus and Methods

Acetone, benzene and ethylacetate employed as solvents in all experiments have been obtained by dehydration on silica gel, followed by rectification on a column with 25 theoretical plates starting from Merck solvents. The distillate portions, taken on a temperature domain of 0.02 degrees, evidenced the refractive index values (n_D^{25}), as compared to those presented in the specialized literature [14], comprised in Table 1.

Fig. 1 presents the principal diagram of the employed apparatus, in which recirculation and spraying of the thermometer with a vapour – liquid mixture brought on the thermometer with a Cottrell pump, occur. Devices equipped with Cottrell pump are most frequently employed [12].

Constituent parts of the apparatus presented in the figure are: A – electrically

Table 1

Comparative Refractive Index

Solvent	Acetone	Benzene	Ethylacetate
$(n_D^{25})_{exp}$	1.35610	1.4978	1.37001
$(n_D^{25})_{[14]}$	1.35609	1.4979	1.36990

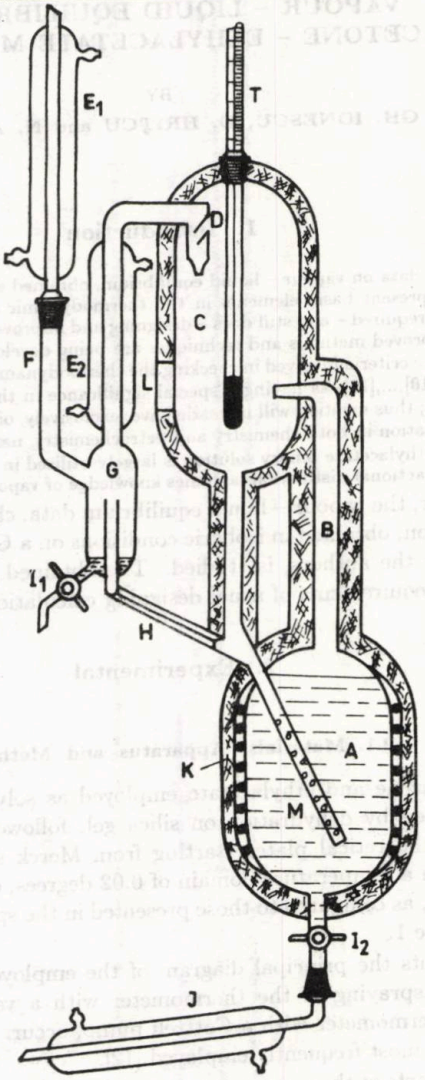

Fig. 1

heated still, B – Cottrell pump, T – thermometer, C – chamber for the establishment of the vapour – liquid equilibrium, D – drop separator, E_1 and E_2 – reflux refrigerators, F – line for atmospheric contact, G – receiver for condensate, equipped with overflow device, H – capillary tube for the condensates return, I_1 and I_2 – taps, J – descending refrigerator for taking over of the solution sample from the still, K – thermal isolation, L – window and M – tube with holes.

The main features of the apparatus are: compact shape and verticality, a new shape of the drop separator, utilization of the M holed tube (for rapid homogenization of the condensate with the still solution), attachement of the descending refrigerator J (for preserving the concentration of the still sample through adequate cooling). The supply design, the external electrical heating which prevents possible thermal degradations, the low time required for attaining the practical vapour – liquid equilibrium (about 30 min. after closing the solution–condensate circuit) represent real advantages in the utilization of such device in the study of vapour – liquid equilibrium.

Running of this device is, practically, identical to that described in the literature [15]. Removal of the liquid containing hose, determined by the necessity of placing the thermometer bulb and, consequently, the sensible reduction of time required to reach the vapour – liquid equilibrium may be quite correctly explained by the formulation given by K h a r e t n i k o v [16].

The composition of the vapour – liquid equilibrium phases has been established by refractometric analysis, both for testing the proposed apparatus and for the study of the acetone–ethylacetate solutions. The method necessitates quite low amounts of distillate and residues (below 0.5 mL), which – being collected from the system – do not alter, practically, the solution under study, of about 100 mL.

2.2. Testing of the Installation's Performances

For checking the apparatus we present, a binary solution has been employed (containing acetone as one of the constituents), on which several literature data were available [17],...,[21]. The idea that an acetone – benzene solution has been selected as test solution may be explained, too, by the fact that we intend to initiate studies, on the other binary solutions containing acetone. We shall refer mainly to the acetone–esters systems, on which quite scarce vapour – liquid equilibrium data are available.

The vapour – liquid equilibrium has been realized for six samples, on employing the apparatus from Fig. 1. The experimental data obtained have been compared with some of the literature information available [17],...,[21], a good agreement between them being recorded [17], [18], which might be explained both by the utilization of the apparatus described above, equipped with a Cottrell pump and a recirculation system, and by application of suitable experimental procedures. Other literature data [19],...,[21] are sensibly differing, both among them and as compared to ours and to those in literature [17], [18]. The above mentioned literature data are also systematized in the reference list accompanying the studies [22], [23]. Table 2

presents both our and literature data for acetone–benzene system.

The significant differences observed between the experimental data of various authors are indicative of the difficulties to be faced in the study of vapour – liquid equilibria; they are induced by different devices used, the working mode applied, the purity of the utilised solvents, etc.

Table 2

Comparative Experimental Data for Acetone–Benzene System (acetone as comp. 1); p=760 Torr

t_{nf}, [°C]	76.5	66.7	65.0	63.8	62.3	59.5	Ref.
x_1	0.050	0.300	0.375	0.436	0.517	0.706	[17]*)
y_1	0.140	0.515	0.580	0.632	0.696	0.817	
x_1	0.095	0.400	0.470	0.522	0.605	0.808	[19]*)
y_1	0.240	0.595	0.645	0.682	0.732	0.870	
x_1	0.077	0.332	0.402	0.463	0.547	0.725	[20], [21]
x_1	0.052	0.305	0.380	0.440	0.505	0.710	Ours
y_1	0.135	0.520	0.584	0.650	0.690	0.815	data
$\%\delta, (x_1)$**)	4.33	1.67	1.33	0.92	−2.32	0.57	
$\%\delta, (y_1)$	−3.57	0.97	0.69	2.85	−0.86	−0.39	

*) Numerical data were obtained by interpolationon the t_{nf} vs. x_1 and t_{nf} vs. y_1 curves.

**) Calculated in comparison with data from [19].

3. Results and Discussions

As far as we know, no tables and diagrams given in literature contain vapour – liquid equilibrium data for the acetone (*1*)–ethyl–acetata (*2*) solution; on employing above mentioned equipment, we have initiated a study of this binary solution under isobaric conditions (at 760 Torr).

The vapour – liquid equilibrium has been obtained for 12 acetone–ethylacetate solutions. Measurements of the refractive index for both the distillate and the residuum together the calibration curve n_D^{25} vs. x_1 were used for the two phases composition determination, while application of the van L a a r theoretical equations permited to calculate the phases composition, at equilibrium temperature, for all twelve solutions considered. Table 3 lists both the experimentally and calculated compositions.

The van L a a r equations have been applied in the form of the following expressions:

$$(1) \qquad x_1 = \frac{1 - e^{\lambda_2}}{e^{\lambda_1} - e^{\lambda_2}}, \qquad (2) \qquad y_1 = \frac{1 - e^{\lambda_2}}{1 - e^{\lambda_1 - \lambda_2}},$$

$$(3) \quad \lambda_1 = \frac{\Delta_v H_{m01}}{R}\left(\frac{1}{T_{f01}} - \frac{1}{T_{fs}}\right), \qquad (4) \quad \lambda_2 = \frac{\Delta_v H_{m02}}{R}\left(\frac{1}{T_{f02}} - \frac{1}{T_{fs}}\right),$$

Table 3
Experimental and Theoretical Data of the Vapour – Liquid Equilibrium for the Acetone–Ethylacetate Solutions

t_{nf} °C	Experimental		van L a a r eq.	
	x_1	y_1	x_1	y_1
77.10	0	0	0	0
74.94	0.045	0.126	0.078	0.140
72.30	0.127	0.240	0.179	0.297
69.50	0.210	0.388	0.295	0.449
66.71	0.334	0.530	0.421	0.587
64.70	0.420	0.636	0.520	0.682
62.40	0.560	0.732	0.636	0.776
60.80	0.656	0.800	0.724	0.839
59.70	0.716	0.852	0.787	0.881
58.90	0.802	0.885	0.834	0.910
58.15	0.850	0.912	0.879	0.936
57.15	0.928	0.964	0.942	0.970
56.74	0.953	0.977	0.968	0.984
56.20	1	1	1	1

where: $\Delta_v H_{m0i}$ – latent molar vaporization heat values of the pure compounds, T_{f0i} – boiling temperatures of pure compounds at 760 Torr and T_{fs} – boiling temperature of the solution at 760 Torr.

4. Conclusions

1. The described apparatus is equipped with a Cottrell pump, being thus similar with most of the devices employed in the study of the vapour – liquid equilibrium, under isobaric conditions, but, unlike of these, is provided with some improvements.

2. No comparable literature data have been available for the acetone–ethylacetate solution, which makes us believe that ours is, probably, one of the few contributions devoted to this binary solution.

3. Sensible and systematic differences do exist between the experimental and theoretical recorded values, which is an indication of the non-ideal properties characterizing the acetone–ethylacetate solution. As $(x_1)_{exp} < (x_1)_{van\ Laar}$, the deviations of this solution from the properties of an ideal solution are considered as positive. Such a hypothesis is quite plausible, if one takes into account the possibility of strong hydrogen bonds formation between the molecules or, at least, the existance of a significant dipole–dipole interactions between them, in the pure components, in comparison with these interactions between the molecules in solution.

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ECHILIBRE LICHID – VAPORI PENTRU AMESTECURI ACETONĂ – ACETAT DE ETIL

(Rezumat)

Se studiază echilibrul lichid–vapori în condiţii izobare. S-a construit un aparat, bazat pe principiul recirculării, prevăzut cu pompă Cottrell, pentru evitarea supraîncălzirii fazei lichide. Principiul de construcţie al aparatului este cu geometrie verticală, performanţele sale fiind comparabile cu cele obţinute cu aparate care funcţionează pe acelaşi principiu. S-a studiat echilibrul lichid–vapori pentru soluţii de acetonă–acetat de etil. Rezultatele experimentale obţinute pun în evidenţă faptul că acest sistem este neideal şi prezintă abateri pozitive faţă de soluţiile perfecte.

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STUDIES ON THE ZINC BEHAVIOUR IN BYPRODUCTS OF THE METALLURGICAL INDUSTRY

BY
FLORIN BANDRABUR, MARIA APOSTOLESCU and ŞT. IVĂŞCAN

1. Introduction

In the technology of copper obtaining by the pyrometallurgical procedure volatile dusts results which are captured in the systems for dust collection from technological gases.

The requirements of working these volatile dusts is imposed by the nature and concentration of contained elements: Pb (20...25%); Zn (25...30%); As (12...17%); Cu (0.5...1%); Cd (0.5...1%).

To analyse the elements contained in volatile dusts a complex process of working was developed in cooperation with U.C.P.M.N., Baia Mare.

2. Theoretical Considerations on the Process of Electrolytic Extraction of Zinc

The volatile dusts are submitted to an acid leaching process. The component elements separate in various stages resulting finally an acid solution containing Zn^{2+} ions. In the present paper some theoretical and experimental aspects of the electrolytic separation of zinc from the acid solutions are reported.

The processes taking place at the two electrodes are:

(1) $$\text{at anode}: \quad 2H_2O \rightarrow O_2 + 4H^+ + 4e^-,$$

(2) $$\text{at cathode}: \quad Zn^{2+} + 2H^+ + 4e^- \rightarrow Zn + H_2.$$

The overall equation for the electrolysis cell can be written as:

(3) $$Zn^{2+} + 2H_2O \rightarrow O_2 + Zn + 2H^+ + H_2.$$

To describe quantitatively the process of zinc separation the conversion degree was defined as:

$$\eta_{Zn^{2+}} = \frac{n^0_{Zn^{2+}} - n_{Zn^{2+}}}{n^0_{Zn^{2+}}} = \frac{n_{Zn}}{n^0_{Zn^{2+}}}. \tag{4}$$

The correlation between the conversion degree and the current yield is given by the equation:

$$\eta_{Zn^{2+}} = \frac{A_{Zn} I \tau}{2 n^0_{Zn^{2+}} F} r_c. \tag{5}$$

The scheme of the cathode process is given in Fig. 1.

$$-T_{Zn^{2+}_{[\,]_l}} \rightarrow -\mathrm{Ads}_{Zn^{2+}_{[\,]_s}} \rightarrow -r_2 \rightarrow -N_{Zn_{[\,]_s}} \rightarrow$$

$$-T_{H^+_{[\,]_l}} \rightarrow -\mathrm{Ads}_{Al_{[\,]_s}} \rightarrow -r_2 \rightarrow -N_{H_{2[\,]_g}} \rightarrow -\mathrm{Des}_{H_2O_{[\,]_g}} \rightarrow -T_{H_{2[\,]_g}} \rightarrow$$

Fig. 1.– The scheme of the cathode process.

The cathode process belongs to a process class of the form: adsorption–reaction–nucleation. Starting from the structure of the cathode process (Fig. 1) and considering the model of completely immersed plate as one of contact between phases [1], the following mathematical models have been derived [2]:

a) A mathematical model corresponding to the macrokinetic process of transfer of Zn^{2+} ions through solution:

$$\tau = \frac{1}{K_{T_{[]l}}} \cdot \frac{\rho^*_{Zn} h}{C^0_{Zn^{2+}}} \cdot \frac{\eta_{Zn^{2+}}}{1 - \eta_{Zn^{2+}}}. \tag{6}$$

b) A mathematical model corresponding to the macrokinetic process of conversion (adsorption–reaction–nucleation):

$$\tau = \frac{1}{K_r} \cdot \frac{\rho^*_{Zn} h}{C^0_{Zn^{2+}}} \cdot \frac{\eta_{Zn^{2+}}}{1 - \eta_{Zn^{2+}}}. \tag{7}$$

3. Analysis of Process Based on the Experimental Data

The experimental data carried out on laboratory equipment were aimed to settle the optimal parameters for the process of electrolytic extraction of zinc from the acid solutions resulting from the working of volatile dusts. The solution submitted to the electrolytic extraction contained 110...120 g/l Zn^{2+} and 40 g/l H_2SO_4. The

work parameters in the electrolysis cell were the following: a) current density at cathode, 300...325 A/dm^2; b) cell voltage, 3.7...4 V.

For the runs Pb anodes and Al cathodes have been used.

The measurements ware taken at constant temperature (15°, 30°and 45°C).

The anodes and cathodes have been polished, degrased and scaled according to the nature of the material they were manufactured in.

Experimentally the variation in time of Zn^{2+} ion concentration has been determined as well as of conductivity and pH (Figs. 2, 3 and 4).

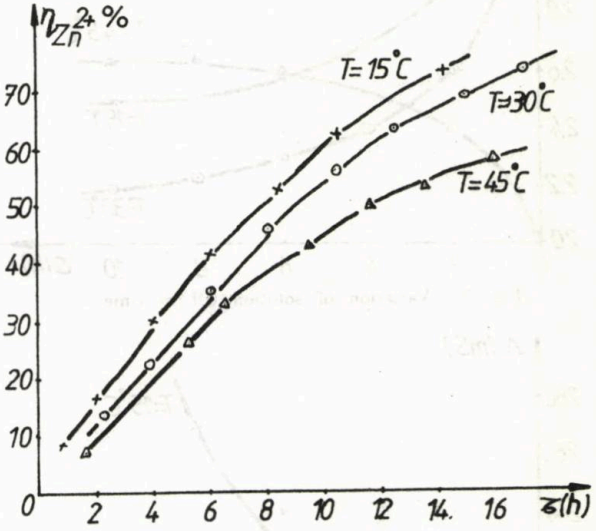

Fig. 2.– $\eta_{Zn^{2+}}$ vs. τ kinetic curves.

Based on equation (5) the dependence of current yield versus the solution concentration in Zn^{2+} ions has been plotted (Fig. 5).

The obtained results lead to the conclusion that the structure of cathode deposit depends on the initial concentration of Zn^{2+} ions in the solution. Thus the deposits obtained from concentrated solutions ($C^0_{Zn^{2+}} = 120$ g/l) are less smooth, the possibility existing of detachment of Zn crystalls, which results in diminishing the final separation degree. This disadvantage can be avoided by working with more diluted solutions ($C^0_{Zn^{2+}} = 80$ g/l).

Based on kinetic curves represented in Fig. 2 by the method of horizontal sections [2], [3], the dependence $\ln 1/\tau$ vs. $1/T$ was plotted (Fig. 6). Since the experimental values lie on straight lines the conclusion can be drawn that the process develop according to a single macrokinetic mechanism.

From the slopes of the lines the apparent energy of activation was calculated (values comprised between 2870 and 3710 kcal/mole were found).

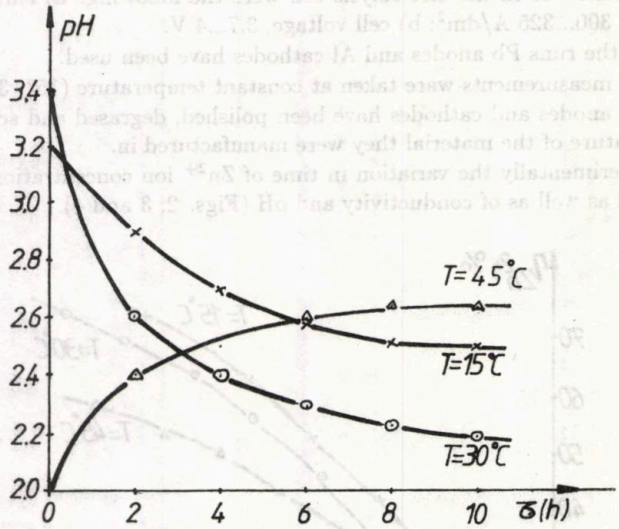

Fig. 3.– Variation of solution pH in time.

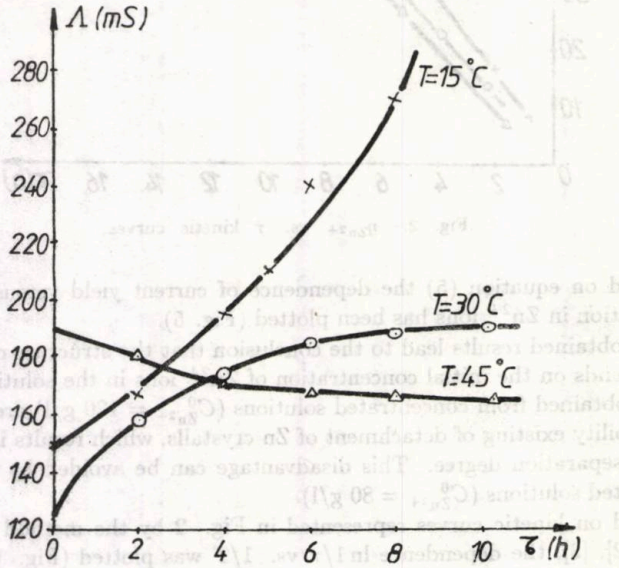

Fig. 4.– Variation of solution conductivity in time.

By means experimental results the mathematical data were checked (Eqs. (6) and (7)). As can be seen in Fig. 7 the experimental data check the liniar depen-

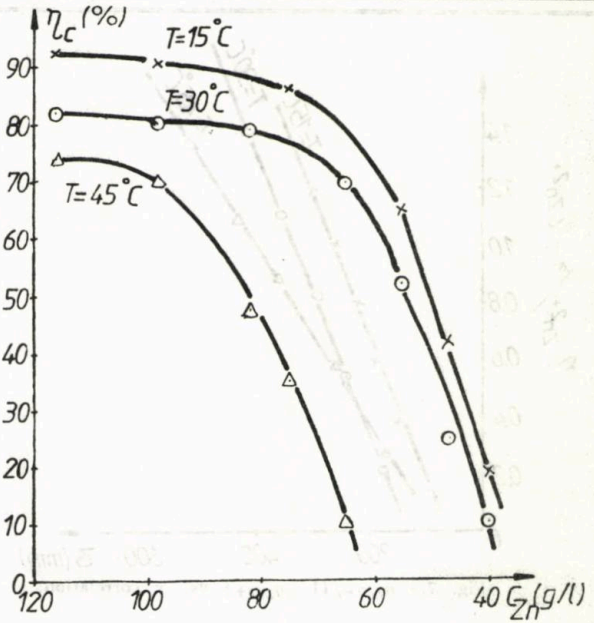

Fig. 5.– Dependence of current yield on the solution concentration in Zn^{2+} ions.

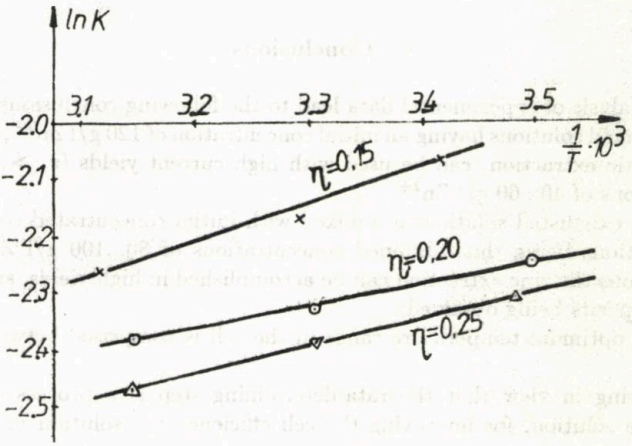

Fig. 6.– $\ln 1/\tau$ vs. $1/T$ correlation.

dences $\eta_{Zn^{2+}}$ vs. τ.

By correlating the apparent energy of activation with the mathematical models

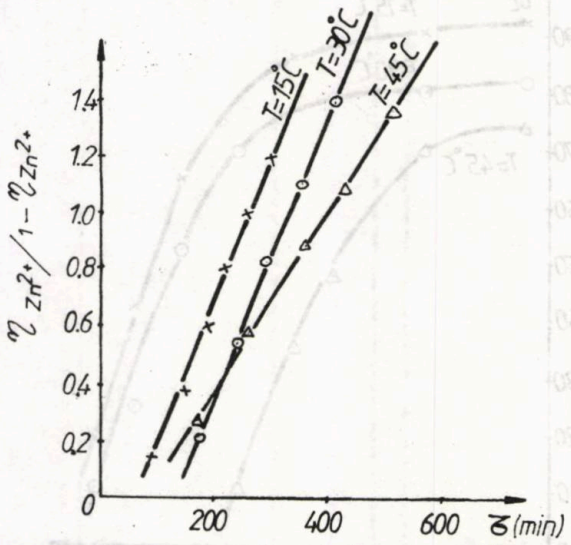

Fig. 7.– $\eta_{Zn^{2+}}/(1-\eta_{Zn^{2+}})$ vs. τ correlation.

the conclusion can be drawn that the transfer of Zn^{2+} ions through solution towards the cathods surface is the rate determining step.

4. Conclusions

The analysis of experimental data lead to the following conclusions:

a) The acid solutions having an initial concentration of 120 g/l Zn^{2+}, submitted to electrolytic extraction, can be used with high current yields ($r_c > 0.8$) up to concentrations of 40...60 g/l Zn^{2+}.

b) The exhausted solutions are mixed with initial concentrated solutions recycled solutions being thus obtained concentrations of 80...100 g/l Zn^{2+}; from these solutions the zinc extraction can be accomplished in high yields, smooth and compact deposits being obtained.

c) The optimum temperature range in the cell is comprised between 20°and 30°C.

d) Having in view that the rata-determining step is a process of transfer through the solution, for improving the cell efficiency the solution mixing is required.

Notations

A_{Zn} – atomic weight of zinc;

$n^0_{Zn^{2+}}$, $m^0_{Zn^{2+}}$ – number of moles and mass of Zn^{2+} ions in initial solution, respectively;

F – Faraday constant;

ρ^*_{Zn} – molar density of zinc, [kmole/m^3];

$K_{T_{[\ ]l}}$ – coefficient of transfer in liquid phase, [m/s];

K_r – reaction rate constant, [s^{-1}];

$C^0_{Zn^{2+}}$ – concentration in Zn^{2+} ions of initial solution, [kmole/m^3];

Ads – adsorption process on the cathode surface;

T – symbol of the transfer processes in a phase.

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CERCETĂRI PRIVIND RECUPERAREA ZINCULUI DIN SUBPRODUSE ALE INDUSTRIEI METALURGICE

(Rezumat)

S-a analizat procesul de separare a zincului prin electroliză din soluţii provenite din subproduse ale metalurgiei cuprului.

Pe baza reacţiilor de electrod s-au stabilit mecanismul procesului şi modelele macrocinetice corespunzătoare.

Din datele experimentale s-a calculat energia aparentă de activare şi s-au verificat modelele matematice; s-a stabilit că stadiul de viteză limitativ pentru procesul catodic îl reprezintă transferul ionilor Zn^{2+} prin electrolit către suprafaţa electrolitului.

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ANALYSE DE L'INSTALLATION NORSK – HYDRO D'OBTENTION DES NITROPHOSPHATES

III. LES PROCESSUS COMPOSANTS: AMMONISATION, CONCENTRATION, DOSAGE KCl ET GRANULATION

PAR

CAROLINA HAGIU et RODICA DIACONESCU

1. Introduction

L'élaboration des modèles de bilan de masse et leur utilisation pour l'analyse, sur ordinateur, d'un processus technologique constitue une méthode de conduite rigoureusement scientifique du processus et d'établissement des moyens de le perfectionner. Dans des travaux antérieus [1], [2] on a élaboré des modèles de bilan de masse pour les processus composants et pour le processus technologique „désagrégation nitrique"; à partir de ces modèles et utilisant la technique moderne de calcul nous avons établi les conditions technologiques optimales d'action de l'installation industrielle fonction de la qualité de la matière première phosphatée pour l'obtention de la solution mère de composition chimique constante – condition absolument nécessaire à l'obtention des engrais N–P et N–P–K de la qualité souhaitéé.

Dans ce qui suit on élabore et vérifie les modèles de bilan de masse pour les processus composants: ammonisation, concentration, dosage KCl et granulation.

2. Modèles de bilan de masse pour les processus composants

Le processus technologique „obtention des engrais N–P et N–P–K", présenté dans la Fig. 1, consiste dans l'ammonisation de la „solution mère" dans la concentration de la solution (respectivement de la suspension) obtenue, suivie par la granulation de la pâte d'engrais, avec ou sans supplément de KCl.

Dans l'élaboration des modèles de bilan de masse pour les processus composants on a appliqué la méthode connue [3] et on a défini et utilisé des rapports phasiques qui mettent en corrélation les débits de masse des produits finis et intermédiaire au débit de masse de roche phosphatée et sa qualité. On obtient ainsi des modèles de bilan sous une forme adéquate à l'analyse sur ordinateur du processus technologique.

La neutralisation de la „solution mère" se réalise avec de l'ammoniac gazeux pur en trois étapes: la préneutralisation, la neutralisation I et la neutralisation

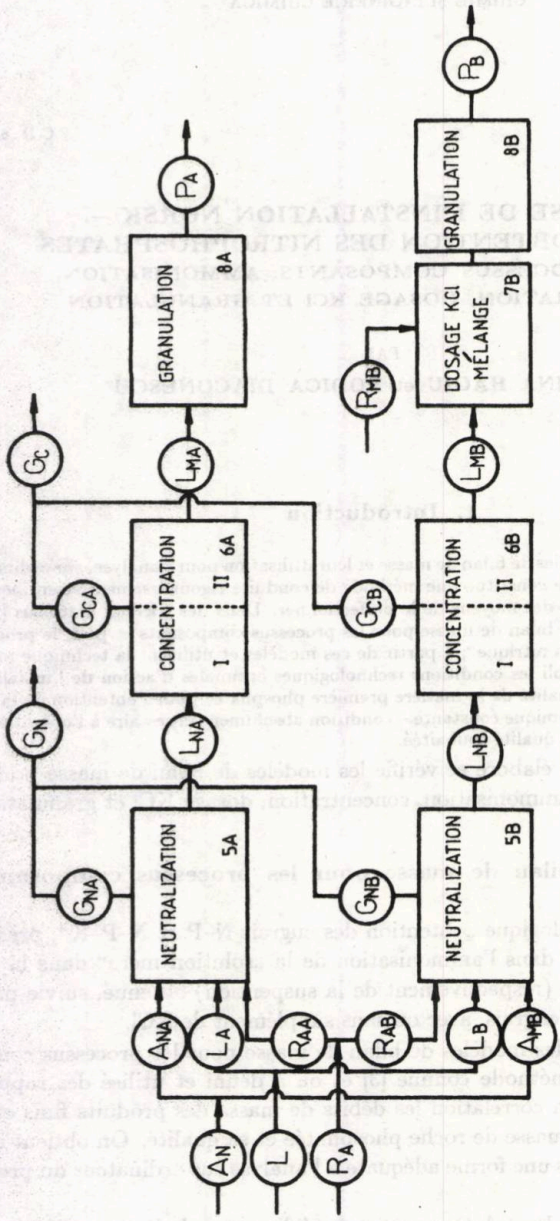

Fig. 1.– Schéma bloc du processus technologique d'obtention des engrais N–P et N–P–K.

II, à la fin desquelles on obtient une suspension d'engrais N–P. Pour la correction du rapport N/P dans les engrais obtenus, dans le processus de préneutralisation on introduit aussi une solution d'azotate d'ammonium résultée de la conversion du $Ca(NO_3)_2$. Le processus global de neutralisation de la solution mère est exprimé par l'équation caractéristique:

$$[H_3PO_4 + HNO_3 + Ca(NO_3)_2 + HF + CO_2 + H_2O + A'']_l^I +$$
$$+[NH_4NO_3 + H_2O]_{l_4^0} + [NH_3]_{g_5^0} \rightarrow [NH_4H_2PO_4 + (NH_4)_2HPO_4 +$$
$$+NH_4NO_3 + CaHPO_4 + Ca_3(PO_4)_2 + CO_2 + CaF_2 + H_2O + A'']_{l_5} +$$
$$+[H_2O + NH_3]_{g_5}$$

Les processus de transformation indépendants sont:

1. $HNO_3+NH_3=NH_4NO_3$;
2. $H_3PO_4+NH_3=NH_4H_2PO_4$;
3. $2HF+Ca(NO_3)_2+2NH_3=CaF_2+2NH_4NO_3$;
4. $Ca(NO_3)_2+NH_4H_2PO_4+NH_3=CaHPO_4+2NH_4NO_3$;
5. $3CaHPO_4+2NH_3=Ca_3(PO_4)_2+(NH_4)_2HPO_4$;
6. $H_2O_{[]l} \rightleftharpoons H_2O_{[]g}$.

Les équations de bilan de masse pour le processus d'ammonisation sont présentées dans le Tableau 1.

La composition chimique de la solution et des gaz résultant de l'ammonisation est calculée a l'aide des équations:

$$\begin{aligned}
&\overline{X}^{s.a}_{P_{[]l_5}} = \frac{1}{L_N} 0,85 L_M \overline{X}_{P_{[]l_6}}, \quad \overline{X}^{s.a.c}_{P_{[]l_5}} = \frac{1}{L_N} 0,98 L_M \overline{X}_{P_{[]l_6}}, \\
&\overline{X}_{CO_2{}_{[]l_5}} = \frac{1}{L_N} \overline{X}^I_{CO_2{}_{[]l}}, \quad \overline{X}_{A''_{[]l_5}} = \frac{1}{L_N} L \overline{X}^I_{A''_{[]l}}, \\
&\overline{X}_{H_2O_{[]l_5}} = L \overline{X}^I_{H_2O_{[]l}} + A_N (1 - \overline{X}^0_{NH_4NO_3}) - G_N (1 - 1,2142 \overline{X}_{N_{[]g_5}}), \\
&\overline{X}_{N_{[]g_5}} = L \overline{X}^I_{N_{[]l}} + 0,35 A_N \overline{X}^0_{NH_4NO_3} + 0,823 R_A \overline{X}^0_{NH_3} - L_N \overline{X}_{N_{[]l_5}}.
\end{aligned} \tag{1}$$

La concentration de la solution phosphonitrique se réalise en deux étapes et on obtient une suspension (une pâte) d'engrais, ayant un faible contenu d'humidité à partir de laquelle on obtient les engrais N–P et N–P–K. Les équations caractéristiques du processus de concentration et des processus de transformation sont:

$$[NH_4H_2PO_4 + (NH_4)_2HPO_4 + NH_4NO_3 + CaHPO_4 + Ca_3(PO_4)_2 +$$
$$+CaF_2 + CO_2 + H_2O + A'']_{l_5} \rightarrow [NH_4H_2PO_4 + (NH_4)_2HPO_4 +$$

Tableau 1

Équations de bilan de masse pour le processus d'amonization

Matières entrées			Matières résultées		
Phase	Composant	Équations de bilan	Phase	Composant	Équations de bilan
Solution mère $[\,]_l^I$	H_3PO_4	$m_{H_3PO_4} = 3,161 m^I_{[]_l} \overline{X}^I_{P[]_l}$	Liquide $[\,]_{l_5}$	$NH_4H_2PO_4$	$m_{MAP} = m^I_{[]_l}(3,7096\overline{X}^I_{P[]_l} - 2,875\overline{X}^I_{Ca[]_l} + 3,0263\overline{X}^I_{F[]_l} + +16,422\overline{X}^I_{N[]_l}) + m_{[]_{l_5}}(3,7096\overline{X}^{s.a.}_{P[]_{l_5}} + 8,2142\overline{X}_{N[]_{l_5}} + +1,8548\overline{X}_{P[]_{l_5}} - 1,8548\overline{X}^{s.a.c.}_{P[]_{l_5}}) + 2,875 m^0_{[]_{l_4}} \overline{X}^0_{NH_4NO_3} = A$
	HNO_3	$m_{HNO_3} = 4,5 m^I_{[]_l}(\overline{X}^I_{N[]_l} - 0,7\overline{X}^I_{Ca[]_l})$			
	$Ca(NO_3)_2$	$m_{Ca(NO_3)_2} = 4,1 m^I_{[]_l} \overline{X}^I_{Ca[]_l}$			
	HF	$m_{HF} = 1,052 m^I_{[]_l} \overline{X}^I_{Ca[]_l}$		$(NH_4)_2HPO_4$	$m_{(NH_4)_2HPO_4} = m_{[]_{l_5}}(9,4285\overline{X}_{N[]_{l_5}} - 4,258\overline{X}^{s.a.}_{P[]_{l_5}}) - -18,857 m^I_{[]_l}\overline{X}^I_{N[]_l} - 3,3 m^0_{[]_{l_4}}\overline{X}^0_{NH_4NO_3} = B$
	CO_2	$m_{CO_2} = m^I_{[]_l}\overline{X}^I_{CO_2[]_l}$			
	H_2O	$m_{H_2O} = m^I_{[]_l}\overline{X}^I_{H_2O[]_l}$		NH_4NO_3	$m_{NH_4NO_3} = m^0_{[]_{l_4}}\overline{X}^0_{NH_4NO_3} + 5,7143 m^I_{[]_l}\overline{X}^I_{N[]_l}$
	Inerte	$m''_A = m^I_{[]_l}\overline{X}^I_{A''_{[]_l}}$		$CaHPO_4$	$m_{CaHPO_4} = m^I_{[]_l}(3,4\overline{X}^I_{Ca[]_l} - 3,5789\overline{X}^I_{F[]_l}) - -6,5806 m_{[]_{l_5}}(\overline{X}^I_{P[]_{l_5}} - \overline{X}^{s.a.c.}_{P[]_{l_5}}) = E$
	Total	$m^I_{[]_l} = 0,4366 m^0_{[]_s}\overline{X}^0_{P_2O_5[]_s}/\overline{X}^I_{P[]_l} = = L m^0_{[]_s}$			
Solution NH_4NO_3	NH_4NO_3	$m_{NH_4NO_3} = m^0_{[]_{l_4}}\overline{X}^0_{NH_4NO_3}$		$Ca_3(PO_4)_2$	$m_{Ca_3(PO_4)_2} = 5 m_{[]_{l_5}}(\overline{X}_{P[]_{l_5}} - \overline{X}^{s.a.c.}_{P[]_{l_5}}) = F$
	H_2O	$m_{H_2O} = m^0_{[]_{l_4}}(1 - \overline{X}^0_{NH_4NO_3})$		CaF_2	$m_{CaF_2} = 2,0526 m^I_{[]_l}\overline{X}^I_{F[]_l} = G$
	Total	$m^0_{[]_{l_4}} = A_N m^0_{[]_s}$		CO_2	$m_{CO_2} = m^I_{[]_l}\overline{X}^I_{CO_2[]_l}$
NH_3	NH_3	$m_{NH_3} = m^0_{[]_{g_5}}\overline{X}^0_{NH_3} = R_A m^0_{[]_s}$		H_2O	$m_{H_2O} = m_{[]_{l_5}}\overline{X}_{H_2O[]_{l_5}}$
				Inerte	$m''_A = m_{[]_{l_5}}\overline{X}_{A''_{[]_{l_5}}} = H$
				Total	$m_{[]_{l_5}} = m^I_{[]_l}\overline{X}^I_{P[]_l}/\overline{X}_{P[]_{l_5}} = L_N m^0_{[]_s}$
Total		$m_T = m^I_{[]_l} + m^0_{[]_{l_4}} + m^0_{[]_{g_5}}$	Gas $[\,]_{g_5}$	NH_3	$m_{NH_3} = m^0_{NH_3} + m^I_{[]_l}(1,2134\overline{X}^I_{N[]_l} + 0,4248\overline{X}^I_{Ca[]_l} - 0,5483\overline{X}^I_{P[]_l} - -0,4469\overline{X}^I_{F[]_l}) - m_{[]_{l_5}}(1,2142\overline{X}_{N[]_{l_5}} - 0,5483\overline{X}^{s.a.}_{P[]_{l_5}} + +0,2742\overline{X}_{P[]_{l_5}} - 0,2742\overline{X}^{s.a.c.}_{P[]_{l_5}}) + 0,4245 m^0_{[]_{l_4}}\overline{X}^0_{NH_4NO_3} = I$
				H_2O	$m_{H_2O} = m^I_{[]_l}\overline{X}^I_{H_2O[]_l} + m^0_{[]_{l_4}}(1 - \overline{X}^0_{NH_4NO_3}) - m_{[]_{l_5}}\overline{X}_{H_2O[]_{l_5}} = J$
				Total	$m_{[]_{g_5}} = G_N m^0_{[]_s}$
			Total		$m_I = m_{[]_{l_5}} + m_{[]_{g_5}}$

Observation.

$\overline{X}^{s.a.}_{P[]_{l_5}}$ = fraction soluble dans l'eau;

$\overline{X}^{s.a.c.}_{P[]_{l_5}}$ = fraction soluble dans l'eau et le citrate

$$+NH_4NO_3 + CaHPO_4 + Ca_3(PO_4)_2 + CaF_2 + A'' + H_2O]_{l_6} +$$

$$+[CO_2 + NH_3 + HNO_3 + H_2O]_{g_6},$$

$$H_2O_{[]_l} \rightleftharpoons H_2O_{[]_g}, \quad CO_{2[]_l} \rightleftharpoons CO_{2[]_g}, \quad NH_4NO_{3[]_l} \rightleftharpoons NH_3 + HNO_3.$$

Les modèles de bilan de masse pour le processus de concentration sont présentés dans le Tableau 2. Leur utilisation exige la connaissance des grandeurs: $\overline{X}_{N_{[]_{l_6}}}$, $\overline{X}_{H_2O_{[]_{l_6}}}$, $\overline{X}_{N_{[]_{g_6}}}$ et de celles qui sont indiquées dans [1].

Tableau 2

Équations du bilan de masse pour le processus de concentration

Phase	Composant	Matières résultées
		Équations de bilan
Suspension $N-P_{[]}^{*}{}_{l_6}$	$NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $CaHPO_4$, $Ca_3(PO_4)_2$, CaF_2, Inerte	Sont données dans le Tableau 1
	NH_4NO_3	$m_{NH_4NO_3} = m^0_{[]_{l_4}} \overline{X}^0_{NH_4NO_3} + 5,7143 m^I_{[]_l} \overline{X}^I_{N_{[]_l}} - 2,875(m_{[]_{l_5}} \overline{X}_{N_{[]_{l_5}}} - m^*_{[]_{l_6}} \overline{X}_{N_{[]_{l_6}}}) = C$
	H_2O	$m_{H_2O} = m^*_{[]_{l_6}} \overline{X}_{H_2O[]_{l_6}} = D$
	Total	$m^*_{[]_{l_6}} = m^I_{[]_l} \overline{X}^I_{P_{[]_l}} / \overline{X}_{P_{[]_{l_6}}} = L_M m^0_{[]_s}$
Gas $[]_{g_6}$	NH_3	$m_{NH_3} = 0,607(m_{[]_{l_5}} \overline{X}_{N_{[]_{l_5}}} - m^*_{[]_{l_6}} \overline{X}_{N_{[]_{l_6}}}) \overline{X}_{N_{[]_{g_6}}} = K$
	CO_2	$m_{CO_2} = m_{[]_{l_5}} \overline{X}_{CO_2[]_{l_5}} = M$
	HNO_3	$m_{HNO_3} = 2,25(m_{[]_{l_5}} \overline{X}_{N[]_{l_5}} - m^*_{[]_{l_6}} \overline{X}_{N[]_{l_6}}) = N$
	H_2O	$m_{H_2O} = m_{[]_{l_5}} \overline{X}_{H_2O[]_{l_5}} - m^*_{[]_{l_6}} \overline{X}_{H_2O[]_{l_6}} = O$
	Total	$m_{[]_{g_6}} = G_C m^0_{[]_s}$
Total		$m_T = m^0_{[]_s}(L_M + G_C)$

Le dosage du KCl et le mélange avec la pâte d'engrais N–P (ligne B) est un processus physique dont les équations de bilan sont présentées dans le Tableau 3.

La granulation de la pâte d'engrais N–P (ligne A) et N–P–K (ligne B) se produit en présence du matériel de recyclage. Les équations du bilan de masse pour le processus de granulation, sans prendre en considération la poussière, sont présentées dans le Tableau 4.

3. Conclusions

On a élaboré des modèles de bilan de masse pour le processus chimique et physique de l'installation d'obtention des engrais N–P et N–P–K: neutralisation

Tableau 3

Équations de bilan de masse pour le dosage du KCl

Phase	Composant	Matières entrées — Équations de bilan	Phase	Composant	Matières résultées — Équations de bilan
	$NH_4H_2PO_4$			$NH_4H_2PO_4$	$m_{MAP} = (1-Y)m_{MAP}{}^{\bullet}_{\square_{l_6}}$
	$(NH_4)_2HPO_4$			$(NH_4)_2HPO_4$	$m_{DAP} = (1-Y)m_{DAP}{}^{\bullet}_{\square_{l_6}}$
Sus-	$CaHPO_4$	Sont données		NH_4NO_3	$m_{NH_4NO_3} = (1-Y)[m^0_{\square_{l_4}} \overline{X}^0_{NH_4NO_3} +$
pen-	$Ca_3(PO_4)_2$	dans le			$+5,7143 m^I_{\square_l} \overline{X}^I_{N\square_l} - 2,857(m_{\square_{l_5}} \overline{X}_{N\square_{l_5}} -$
sion	CaF_2	Tableau 2			$- m_{\square^{\bullet}_{l_6}} \overline{X}_{N\square^{\bullet}_{l_6}})]$
$N\text{–}P_{[\,]^{\bullet}_{l_6}}$	Inerte		Pâte	$CaHPO_4$	$m_{CaHPO_4} = (1-Y)m_{CaHPO_4\square^{\bullet}_{l_6}}$
	NH_4NO_3		engrais	$Ca_3(PO_4)_2$	$m_{Ca_3(PO_4)_2} = (1-Y)m_{Ca_3(PO_4)_2\square^{\bullet}_{l_6}}$
	H_2O		N–P–K	H_2O	$m_{H_2O} = (1-Y)\overline{X}_{H_2O\square_{l_6}} m_{\square^{\bullet}_{l_6}}$
	Total		$[\,]^{\bullet}_{l_{7B}}$	CaF_2	$m_{CaF_2} = (1-Y)m_{CaF_2\square^{\bullet}_{l_6}}$
	K_2O	$m_{K_2O} = m^0_{\square_{s_2}} \overline{X}^0_{K_2O}$		K_2O	$m_{K_2O} = m^0_{\square_{s_2}} \overline{X}^0_{K_2O\square_{s_2}}$
$KCl_{\square^0_{s_2}}$	Inerte	$m_{A''} = m^0_{\square_{s_2}} \overline{X}^0_{A''}$		Inerte	$m_{A''} = (1-Y)m_{A''\square^{\bullet}_{l_6}} + m_{\square^0_{s_2}} \overline{X}_{A''\square^0_{s_2}}$
	Total	$m^0_{\square_{s_2}} = R_{MB} m^0_{\square_s}$		Total	$m^{\bullet}_{\square_{l_{7B}}} = (R_{MB} + L_{MB}) m^0_{\square_s}$

Tableau 4

Équations de bilan de masse pour le processus de granulation

Matières résultées					
Ligne *A*			Ligne *B*		
Phase	Composant	Équation de bilan	Phase	Composant	Équation de bilan
Engrais granulé N–P $\square^{II}_{sA}$	$NH_4H_2PO_4$	$m_{NH_4H_2PO_4} = Y m_{NH_4H_2PO_4 \square^{*}_{l6}}$	Engrais granulé N–P–K $\square^{II}_{sB}$	$NH_4H_2PO_4$	$m_{MAP} = (1-Y) m_{MAP \square^{*}_{l6}}$
	$(NH_4)_2HPO_4$	$m_{DAP} = Y m_{DAP \square^{*}_{l6}}$		$(NH_4)_2HPO_4$	$m_{DAP} = (1-Y) m_{DAP \square^{*}_{l6}}$
	NH_4NO_3	$m_{NH_4NO_3} = Y m_{NH_4NO_3 \square^{*}_{l6}}$		NH_4NO_3	$m_{NH_4NO_3} = (1-Y) m_{NH_4NO_3 \square^{*}_{l6}}$
	$CaHPO_4$	$m_{CaHPO_4} = Y m_{CaHPO_4 \square^{*}_{l6}}$		$CaHPO_4$	$m_{CaHPO_4} = (1-Y) m_{CaHPO_4 \square^{*}_{l6}}$
	$Ca_3(PO_4)_2$	$m_{Ca_3(PO_4)_2} = Y m_{Ca_3(PO_4)_2 \square^{*}_{l6}}$		$Ca_3(PO_4)_2$	$m_{Ca_3(PO_4)_2} = (1-Y) m_{Ca_3(PO_4)_2 \square^{*}_{l6}}$
	CaF_2	$m_{CaF_2} = Y m_{CaF_2 \square^{*}_{l6}}$		CaF_2	$m_{CaF_2} = (1-Y) m_{CaF_2 \square^{*}_{l6}}$
	Inerte	$m_{A''} = Y m_{A'' \square^{*}_{l6}}$		K_2O	$m_{K_2O} = m^{0}_{\square_{s2}} \overline{X}^{0}_{K_2O}$
	H_2O	$m_{H_2O} = Y m_{H_2O \square^{*}_{l6}}$		Inerte	$m_{A''} = (1-Y) m_{A'' \square^{*}_{l6}} + m^{0}_{\square_{s2}} \overline{X}^{0}_{A''}$
				H_2O	$m_{H_2O} = (1-Y) m_{H_2O \square^{*}_{l6}}$
	Total	$m^{II}_{\square SA} = L_{MA} m^{0}_{\square_s}$		Total	$m^{II}_{\square SB} = (L_{MB} + R_{MB}) m^{0}_{\square_s}$

avec de l'ammoniaque, concentration, dosage du KCl et granulation, sous une forme accesible à l'utilisation des ordinateurs.

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ANALIZA INSTALAŢIEI NORSK-HYDRO DE OBŢINERE A NITROFOSFAŢILOR
III. Amonizare, concentrare, dozare KCl şi granulare

(Rezumat)

Se continuă analiza funcţionării instalaţiei Norsk-Hydro de obţinere a nitrofosfaţilor în condiţiile utilizării fosforitei de Maroc. Se elaborează şi se verifică modelele de bilanţ de masă pentru procesele componente: amonizare, concentrare, dozare KCl şi granulare, într-o formă adecvată analizei pe calculator a procesului.

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MATHEMATICAL MODELLING OF PROCESS OF PENICILLIN V SEPARATION FROM AQUEOUS PHASE BY REACTIVE EXTRACTION

BY
CORNELIU ONISCU, DAN CAŞCAVAL and VIOLETA LUNGU

1. Introduction

The Penicillin V, obtained by biosynthesis processes, is separated after fermentation from the aqueous phase by means of some laborious extraction and reextraction stages with a high butyl acetate consumption (as solvent) resulting finally in an overall separation yield of 70...75% [1].

In order to eliminate these shortcomings the possibility of the Penicillin V separation from the aqueous phase by means of other procedures was studied, the reactive extraction among them [2]. For the reactive extraction of the Penicillin V was used a glass column with a pulsatory mixer and the extraction agent was the Amberlitte LA-2-butyl acetat mixture.

This paper is aimed to settle a correlation between the separation yield and the variables influencing decisively this process (pH, mixing time, concentration of extracting agent). In this purpose the statistical analysis was used, with the planning of the experiments, the mathematical model describing the reactive extraction of the Penicillin V with Amberlitte LA-2 being developed on this basis. The parameters influencing significantly the separation have been settled by the F i s h e r test and confirmed by the study on the yield variation.

2. Process Modelling

The reactive extraction yield was calculated by means of the relationship:

$$y = \left(1 - \frac{C_r}{C_i}\right) \cdot 100\%,$$

where: C_r – concentration of Penicillin V in the rafined product, [g/l]; C_i – concentration of Penicillin V in the initial aqueous phase, [g/l].

By our studies the influence of the pH, the mixing time of the two phases and the Amberlitte LA-2 concentration in the butylacetate on the separation yield has been followed.

Thus, real values of the process variables were chosen arbitrarily, their limits and coding being given in Table 1.

Table 1
The Limits and Coding of Process Variables

Variable	Code	Variable level			Step
		−1	0	1	
pH	x_1	3	5	7	2
τ, [s]	x_2	15	45	75	30
C_{LA-2}, [g/l]	x_3	6	46	86	40

The following model has been advanced in order to settle the correlation between the obtained separation yield and the above variables:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + \\ + b_{23}x_2x_3 + b_{123}x_1x_2x_3.$$

The experimental matrix is given in Table 2.

Table 2
The Experimental Matrix

Nr. exp.	x_1	x_2	x_3	y_{exp}, [%]	y_{calc}, [%]
1.	−1	−1	−1	87	87
2.	−1	−1	1	91.1	91.1
3.	−1	1	−1	88.2	88.2
4.	−1	1	1	93.1	93.1
5.	1	1	1	77.14	77.14
6.	1	−1	1	76	75.5
7.	1	1	−1	73.14	73.14
8.	1	−1	−1	69	69
9.	0	0	0	92.14	–
10.	0	0	0	92.24	–
11.	0	0	0	92	–
12.	0	0	0	92.3	–

By means of the obtained data the regression coefficients b_j, the sum of the regression coefficient squares $SP(b_j)$ and the experimental error S_r^2 have been estimated according to literature [3], [4] by using the relationships:

$$b_0 = \overline{y}, \quad b_j = \frac{\sum_{i=1}^{8} x_{ji}y_i}{\sum_{i=1}^{8} x_{ji}^2}, \quad b_{jk} = \frac{\sum_{i=1}^{8} x_{ji}x_{ki}y_i}{\sum_{i=1}^{8} x_{ji}^2x_{ki}^2},$$

$$SP(b_0) = \sum_{i=1}^{8} y_i^2, \quad SP(b_j) = b_j \sum_{i=1}^{8} x_{ji} y_i - \frac{\left(\sum_{i=1}^{8} x_{ji}\right) \cdot \left(\sum_{i=1}^{8} y_i\right)}{8}.$$

The experimental error was settled based on the results of the 9...12 runs in the program center by the relationship:

$$S_r^2 = \frac{\sum_{i=1}^{n} (y_i - \overline{y})^2}{n-1}, \quad (n = 4).$$

The obtained values are listed in Table 3.

Table 3
The Obtained Values for the Regression Coefficients

Regression coefficient	Value
b_0	81.83875
b_1	–0.801875
b_2	1.06125
b_3	2.503
b_{12}	0.25875
b_{13}	0.24625
b_{23}	–0.27375
b_{123}	–0.47625

The standard deviation is:

$$S_{yx_1x_2x_3} = 0.3824.$$

In order to check the normal results obtained in the program center the Q test was need. The calculated Q value is [3]:

$$Q = \frac{x_1 - x_2}{R},$$

where: x_1 – uncertain value; x_2 – the closest to the uncertain value; R – amplitude (difference between the most distant values). It follows that:

$$Q = 0.467.$$

From the Table 3, for a certain threshold of 0.05, $Q = 0.77$ was found. Since the calculated value of 0.467 is lower than the tabulated one of 0.77 it follows that the uncertain value of 92% is also a normal one, so that the four yield values obtained in the program center have all of them taken for calculation.

In order to settle the factors influencing decisively the reactive extraction process the F i s h e r test was used. The values of the function F, given in Table 4, were calculated by means of the relation [3]:

$$F = \frac{\mathrm{SP}(b_j)}{S_r^2}.$$

Table 4
The Values of the Function F

F_1	514.40
F_2	9.01
F_3	50.12

For a confidence level of 0.05 and degrees of freedom of 3 and 7, the value $F = 4.35$ was found from the Table 3. Since every calculated value of the function F is higher than the tabulated one it follows that all factors taken into account influence significantly the separation.

Hence, the regression equation may be written as:

$$y = 81.83875 - 8.01875x_1 + 1.06125x_2 + 2.503x_3 + 0.25875x_1x_2 + \\ + 0.24625x_1x_3 - 0.27375x_2x_3 - 0.47625x_1x_2x_3.$$

The limits between which the yield values, calculated by the regression equation, oscillate around the experimental value, are determined by means of the relation:

$$y \pm tS_{yx_1x_2x_3}.$$

The t values are to be found in the tables for Student distribution [3], for a confidence threshold of 0.05 and 7 degrees of freedom namely:

$$t = 2.365 \quad \text{and} \quad y_{\text{icalc}} = \pm 0.9043.$$

The overall influence of the factors under consideration is estimated by means of the value of the multiple correlation coefficient:

$$r_{yx_1x_2x_3} = \sqrt{1 - \frac{S^2_{yx_1x_2x_3}}{S_y^2}},$$

where:

$$S_y^2 = \frac{\sum_{i=1}^{n}(y_i - \overline{y})^2}{n - (k+1)}$$

denotes the dispersion of the individual values, y_i, around the mean value for the 12 runs. The value of $r_{yx_1x_2x_3} = 0.999$, resulting by calculation, would suggest

a close correlation between the experimental values and the regression equation. The value $r^2_{yx_1x_2x_3} = 0.998$ indicates the performance of the reactive extraction of Penicillin V from the aqueous phase by Amberlitte LA-2, under the experimental conditions, to be influenced in a 99.8% extent by the pH value, the mixing time and the Amberlitte LA-2 concentration in butyl acetate, the rest being due to other factors (the concentration of the Penicillin V in the initial solution, the volume ratio of the aqueous and organic phases, etc.), which have not been taken into account.

3. Determination of Optimum Values of the Parameters under Consideration

To determine the optimum values of the parameters influencing significantly the reactive extraction of Penicilline V by Amberlitte LA-2 an optimization calculation of regressive equation previously derived has been performed. Thus, the gradient method [4] and the following restrictions were taken into account:

$$-1 \leq x_1 \leq 1, \quad -1 \leq x_2 \leq 1, \quad -1 \leq x_3 \leq 1, \quad \text{and} \quad y \leq 100\%.$$

The founded optimum is situated on the boundary, the optimum values being in this case:

$$x_1 = -1, \quad x_2 = 1, \quad x_3 = 1.$$

With these values the parameter decoding was made and the following values resulted:

$$\text{pH} = 3, \quad \tau = 75 \text{ s}, \quad C_{\text{LA}-2} = 86 \text{ g/l},$$

for a maximum yield of

$$y = 93.43\%.$$

4. Conclusions

The separation of Penicillin V from the aqueous phase by reactive extraction with Amberlitte LA-2 in butyl acetate was studied and the empirical mathematical model describing this process derived.

The influence of pH, time of phase mixing, concentration of the extraction agent in the solvent was followed. The conclusion was drawn that these parameters influence the separation process in a 99.8% extent and their optimum values were determined.

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MODELAREA MATEMATICĂ A PROCESULUI DE SEPARARE A PENICILINEI V DIN FAZA APOASĂ PRIN EXTRACŢIE REACTIVĂ

(Rezumat)

Se studiază modelarea matematică empirică a procesului de separare a penicilinei V din soluţii apoase prin extracţie reactivă, utilizând un amestec de acetat de butil şi Amberlit LA-2.

S-a urmărit stabilirea corelaţiei dintre performanţa procesului şi parametrii care-l influenţează: valoarea pH-ului, timpul de amestecare a fazelor, concentraţia Amberlitului LA-2 în acetatul de butil. S-a elaborat o ecuaţie de regresie care descrie dependenţa dintre randamentul extracţiei reactive şi variabilele considerate.

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APPLICATION DE LA MÉTHODE DE L'ÉLECTRODE SÉLECTIVE POUR LE ION SODIUM À LA DÉTERMINATION DU TAUX D'ÉCHANGE DE IONS D'UNE FAUJASITE NaY MODIFIÉE PAR DES CATIONS MULTIVALENTS

PAR

MOHAMED ACHACHE, DJAMEL NIBOU,
ABDELKRIM AZZOUZ, V. HULEA et EMIL DUMITRIU

1. Introduction

L'utilisation de zéolithes comme échangeurs de ions dans la récupération des cations lourds présente un double intérêt qui réside dans la purification des eaux polluantes et l'obtention de catalyseurs potentiels pour certaines réactions chimiques organiques [1],...,[3]. Dans ce contexte, la valeur du taux de fixation d'un cation donné sur la surface zéolithique est souvent déduite de la détermination du taux de substitution des ions sodium.

Parmi les différentes techniques utilisées jusqu'à présent, telles l'absorbtion atomique, la fluorescence X, la spectrophotométrie, rares sont celles qui permettent de suivre l'évolution du taux d'échange de ions *in situ*, sans purification ni préparation préalables de l'échantillon à analyser. Dans cet ordre d'idées, l'utilisation de la méthode à ions sélective peut permettre de doser le ion sodium libéré par la zéolithe dans la solution imprégnante en présence même du cation de substitution.

Le présent travail s'est proposé, dans une première étape, de déterminer les constantes de sélectivité d'une électrode à membrane liquide sensible aux ions sodium, en présence de l'élément dont il faudrait étudier l'effet. Afin de mieux cerner le domaine d'applicabilité de la méthode, des cations appartenant à différents groupes de la classification périodique, tels les ions cobalt, strontium, lanthane, cerium, thallium, plomb et uranyle, ont été étudiés.

2. Partie expérimentale

Un potentiomètre PHN 81 et une cellule METHROHM à deux électrodes (comportant une électrode spécifique aux ions sodium du type PNA-V3/TACUSSEL et une électrode de référence à base de Ag/AgCl du type TACUSSEL) ont été utilisés.

Des nitrates divers de cobalt, strontium, lanthane, cérium, thallium, plomb ou d'uranyle de pureté analytique ont servi à préparer les solutions. Pour la détermination des constantes de sélectivité, chaque série de solutions étalons contient une concentration fixe de 10^{-2} M en cation multivalent et différentes concentrations en ions sodium variant de 10^{-5} M à 1 M. Chaque solution est analysée dans une cellule thermostatée à 70°C sous agitation magnétique permanente et à

un pH acide de l'ordre de 2,5...3,5.

L'applicabilité de la méthode à la détermination du taux d'échange de ions a été vérifiée en présence d'une faujasite Y imprégnée par une solution de nitrate de cérium dans les mêmes conditions que précédemment.

3. Résultats et discussion

La littérature spécialisée [4], [5] signale que seules des concentrations importantes en ions Ag^+ peuvent gêner la détermination du sodium. Ainsi, dans ce type de mesure, il est recommandé d'utiliser une électrode de référence à base de Ag/AgCl.

Des mesures potentiométriques ont été effectuées sur chaque série de solutions ayant des concentrations connues. Les résultats obtenus ont permis d'établir des courbes d'étalonnage exprimant la variation du potentiel mesuré dans chaque solution en fonction de la concentration en ions sodium en présence du cation multivalent considéré [6]. Ces courbes ont permis, à leur tour, d'établir des graphiques de variation de ce potentiel en fonction de $-\log(a_{\mathrm{Na}})$ ou $p\mathrm{Na}$ ($a_{\mathrm{Na}+}$ est l'activité du ion Na^+ considérée égale à la concentration). Selon la Fig. 1, tous les graphiques ont pratiquement la même allure: ils comportent deux parties linéaires et une partie curviligne intermédiaire ce qui permet d'appliquer le modèle de N i k o l s k y représenté par l'équation [4]:

$$E = \mathrm{Cte} + \frac{RT}{z_{\mathrm{Na}+\mathrm{F}}} \ln\left(a_{\mathrm{Na}+} + K a_M \frac{z_{\mathrm{Na}+}}{z_M}\right). \tag{1}$$

La première partie, linéaire, correspond aux concentrations élevées en sodium. Elle est caractérisée par l'équation:

$$E = \mathrm{Cte} + \frac{RT}{z_{\mathrm{Na}+\mathrm{F}}} \ln a_{\mathrm{Na}+}, \tag{2}$$

où $z_{\mathrm{Na}+}$ et $a_{\mathrm{Na}+}$ représentent, respectivement, la charge et l'activité du ion Na^+; l'indice M est relatif au cation en présence duquel le sodium doit être dosé. La seconde partie linéaire correspond, par contre, aux faibles concentrations en sodium. Elle consiste en fait en un palier horizontal (dont le niveau est déterminé par la valeur du rapport $z_{\mathrm{Na}+}/z_M$) conformément à la relation:

$$E = \mathrm{Cte} + \frac{RT}{z_{\mathrm{Na}+\mathrm{F}}} \ln\left(K a_M \frac{z_{\mathrm{Na}+}}{z_M}\right). \tag{3}$$

Il existe une certaine proportionnalité entre le niveau du palier et le numéro atomique. Cette proportionnalité a comme conséquence le fait que la constante d'interférence, qui permet d'évaluer l'importance de l'interférence provoquée par

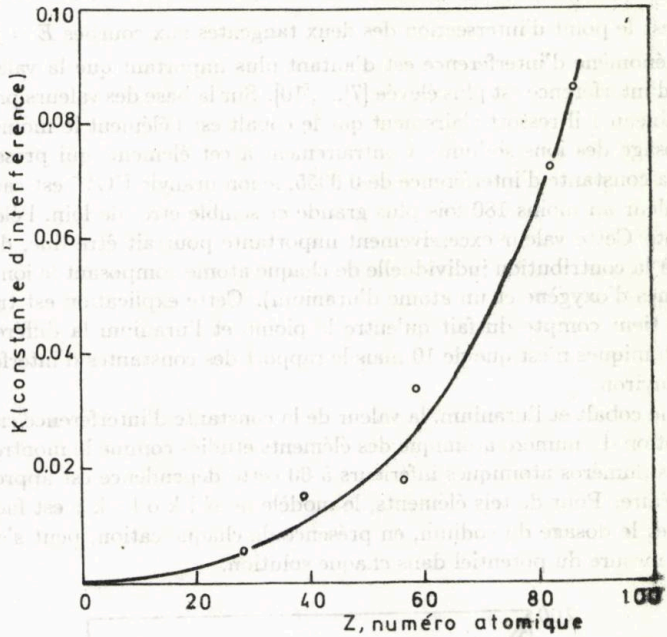

Fig. 1.– Variation du potentiel mesuré en fonction de *p*Na pour les différents cations étudiés.

Tableau 1

Valeurs des constantes d'interférence pour les éléments étudiés

Cation	Numéro atomique	pH de la solution	Constante de sélectivité
Co^{2+}	27	3,5	0,0055
Sr^{2+}	38	3,5	0,0141
La^{3+}	57	3,5	0,0159
Ce^{3+}	58	3,5	0,0316
Tl^{+}	81	3,5	0,0708
Pb^{2+}	85	3,5	0,0850
UO_2^{2+}	O: 8 U: 92	2,5...3,0	1,0000

un cation M donné, est d'autant plus grande que le numéro atomique de ce cation est plus grand (Tableau 1).

Les valeurs de ces constantes d'interférence ont été déterminées par voie graphique à partir des courbes de la Fig. 1 ou par calcul à l'aide de la relation:

$$K = \frac{a_{Na^+_{lim}}}{a_M}, \tag{4}$$

où $a_{Na^+_{lim}}$ est le point d'intersection des deux tangentes aux courbes $E = f(p\text{Na})$.

Le phénomène d'interférence est d'autant plus important que la valeur de la constante d'interférence est plus élevée [7],...,[10]. Sur la base des valeurs présentées dans le Tableau 1 il ressort clairement que le cobalt est l'élément le moins gênant pour le dosage des ions sodium. Contrairement à cet élément, qui présente une valeur de la constante d'interférence de 0,0055, le ion uranyle UO_2^{2+} est caractérisé par une valeur au moins 180 fois plus grande et semble être, de loin, l'élément le plus gênant. Cette valeur excessivement importante pourrait être due, du moins en partie, à la contribution individuelle de chaque atome composant le ion uranyle (deux atomes d'oxygène et un atome d'uranium). Cette explication est très plausible si on tient compte du fait qu'entre le plomb et l'uranium la différence des numéros atomiques n'est que de 10 mais le rapport des constantes d'interférence y est de 12 environ.

Entre le cobalt et l'uranium, la valeur de la constante d'interférence croît avec l'augmentation du numéro atomique des éléments étudiés comme le montre la Fig. 2. Pour des numéros atomiques inférieurs à 60 cette dépendence est approximativement linéaire. Pour de tels éléments, le modèle de N i k o l s k y est facilement applicable et le dosage du sodium, en présence de chaque cation, peut s'effectuer par simple mesure du potentiel dans chaque solution.

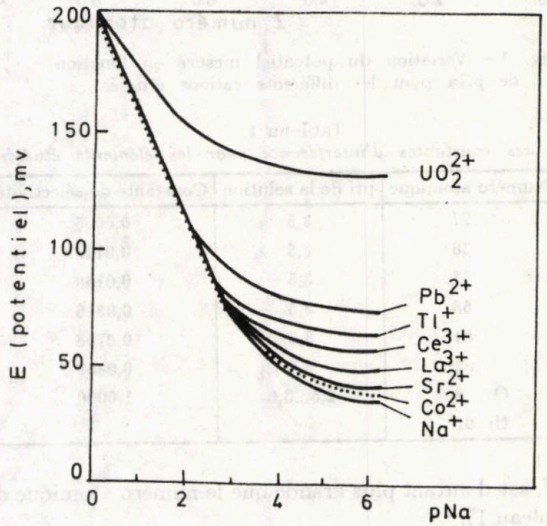

Fig. 2.– Dépendence de la constante de sélectivité en fonction du numéro atomique du cation.

Pour des numéros atomiques supérieurs à 60 les valeurs des constantes d'interférence sont si élevées qu'il serait souhaitable de doser directement l'élément conidéré à l'aide d'une électrode sélective autre que celle destinée au dosage du sodium.

Dans tous les cas l'application de la méthode des électrodes sélectives reste valable pour déterminer soit le taux de substitution du sodium sur des zéolithes du type NaY soit le taux de fixation d'un cation donné sur ces zéolithes.

Le dosage du sodium en présence ou en l'absence de la zéolithe, en équilibre ou non avec la solution imprégnante, ne devrait pas poser de problèmes majeurs. Ce dosage est exclusivement lié à l'équilibre existant entre l'électrode et la solution imprégnante. A titre de vérification, les essais de dosage en „batch" du sodium libéré en présence de la zéolithe échangée et de la solution imprégnante contenant le cation de substitution ont été trés probants. Un taux de substitution de 50% avec des ions Ce^{3+}, préalablement déterminé par absorption atomique, a été trouvé, à l'aide de l'électrode sélective pour les ions sodium en utilisant la courbe d'étalonnage du sodium en présence des ions Ce^{3+}. La différence des résultats obtenus par les deux techniques est de 2,5%.

Le pH et la teneur en cation de substitution sont des facteurs essentiels susceptibles d'influencer la détermination de la concentration en cations sodium d'une solution donnée. La présence de la zéolithe n'est, *a priori*, pas très gênante pour le dosage du sodium libéré. Dans toutes ces investigations le pH a été volontairement ajusté à une valeur comprise entre 3,0 et 3,5 et ceci pour deux raisons évidentes. La première réside dans le fait que les valeurs des constantes d'interférence ne peuvent être comparées que pour des valeurs du pH identiques ou, à défaut, voisines. Dans ce cas, des adjonctions d'acide nitrique sont nécessaires, surtout en ce qui concerne le cobalt et le strontium, pour atteindre la valeur désirée du pH. La deuxième raison est que les opérations d'échange des ions s'effectuent généralement à des valeurs basses du pH des solutions imprégnantes. Ces valeurs du pH sont dues au caractère généralement acide des cations dissous, comme c'est le cas des terres rares et des actinides pour lesquels l'augmentation du pH pourrait provoquer leur précipitation modifiant, ainsi, leurs concentrations.

4. Conclusions

Les courbes tracées et les valeurs des constantes d'interférence sont spécifiques aux conditions opératoires fixées dans la présente étude. La généralisation de ces résultats devra se baser sur des investigations plus poussées. Il est, cependant, permis d'entrevoir l'applicabilité de la méthode à la détermination du taux de fixation des cations relativement légers sur des zéolithes contenant le sodium. Pour les cations lourds, des électrodes sélectives pour ce type d'éléments devraient être utilisées. Dans ce cas il s'agira de doser directement le cation considéré.

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APLICAREA METODEI ELECTRODULUI SELECTIV PENTRU IONUL DE SODIU ÎN DETERMINAREA GRADULUI DE SCHIMB IONIC A FAUJASITULUI NaY MODIFICAT CU CATIONI MULTIVALENŢI

(Rezumat)

Se studiază posibilităţile de dozare a ionilor sodiu în prezenţa cationilor grei, în vederea aplicării sale la determinarea gradului de fixare a acestor cationi pe zeoliţi de tip NaY. Utilizarea metodei electrodului selectiv a permis calcularea constantelor de selectivitate a electrodului în raport cu cationii de cobalt, stronţiu, lantan, ceriu, taliu, plumb şi uranil. Un interes particular a fost acordat influenţei unor parametri asupra dozării sodiului în prezenţa fiecărui cation.

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COMPUTER AIDED MODELLING AND SIMULATION OF POLYCONDENSATION STEP IN POLY(ETHYLENETEREPHTHALATE) SYNTHESIS

BY

SIMION PETROVAN and CONSTANŢA IBĂNESCU

1. Introduction and Objectives

Mathematical modelling and computer aided simulation presents an increasing importance due to the capability and availability of high speed computers.

A mathematical model may consist of a single algebraic equation, sets of equations (algebraic, differential, integral), or any possible combinations of various kinds of equations and mathematical operations, together with appropriately selected initial and boundary conditions. The more complex the model is, the better it will describe or approximate the real system.

The synthesis of poly(ethyleneterephthalate) (PET) involves both chemical reactions and transport phenomena. The mathematical model for the PET synthesis process is non-linear due to the non-linear character of the reaction rates, so that one needs the use of computer for solving and simulating purposes.

In this paper a mathematical model is given, which is used to simulate the polycondensation step in the synthesis of PET, taking into account the diffusion of the micromolecular component (ethylene glycol) (EG) in the melt film. C r a n k - N i c o l s o n method of discretization was used for solving the differential equations with partial derivatives, which are part of the developed model.

2. Mathematical Model

The stoichiometric equation for the second step (ester interchange reaction) can be written in the following form [1],...,[4]:

$$E + E \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Z + G, \tag{1}$$

where:

$E = \mathrm{HO} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{O} - \mathrm{CO} - \ldots$ groups;

$Z = \ldots - \mathrm{COO} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{OOC} - \ldots$ groups;

$G = \mathrm{HO} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{OH}$.

The reaction rates for the three components of the system are as follows:

$$r_e = 2(4k_2zg - k_1e^2), \quad r_g = k_1e^2 - 4k_2zg, \quad r_z = k_1e^2 - 4k_2zg, \tag{2}$$

where e, g and z refers to the molecular species E, G, Z, respectively, and in the right hand side of each equation they have the meaning of concentrations.

The mass balance equations for the three reactant species (that is the equations of continuity) for this case are:

$$\frac{\partial e}{\partial t} = D_e\frac{\partial^2 e}{\partial x^2} + r_e, \quad \frac{\partial g}{\partial t} = D_g\frac{\partial^2 g}{\partial x^2} + r_g, \quad \frac{\partial z}{\partial t} = D_z\frac{\partial^2 z}{\partial x^2} + r_z, \tag{3}$$

where D_e, D_g and D_z are the appropriate diffusion coefficients.

Initial and boundary conditions for the film polycondensation process are:

$$\text{i.c.}: \quad t = 0,\ 0 \le x \le x_0,\ e = e_0,\ g = g_0,\ z = z_0, \tag{4}$$

$$\text{b.c.1}: \quad t > 0,\ x = 0,\ \partial e/\partial x = 0,\ g = g_i,\ \partial z/\partial x = 0, \tag{5}$$

$$\text{b.c.2}: \quad t > 0,\ x = x_0,\ \partial e/\partial x = 0,\ \partial g/\partial x = 0,\ \partial z/\partial x = 0, \tag{6}$$

where g_i is the ethylene glycol concentration at the film interface, e_0, g_0 and z_0 are the initial concentrations of the E, G, and Z molecular species and x_0 is the thickness of the melt film.

3. Algorithm

For solving the system of equations (3) together with initial condition (4) and boundary conditions (5) and (6), C r a n k - N i c o l s o n method was used [5], that is a finite difference method in which the iteration is carried out by calculating the average values of the points in the network, both for concentration variables and reaction rates functions. After discretization by taking $t = n\Delta t$ and $x = m\Delta x$, the system of differential equations (3) leads to the following system with finite differences:

$$\begin{aligned}
\frac{e_{m,n+1} - e_{m,n}}{\Delta t} &= \frac{D_e}{2\Delta x^2}(e_{m-1,n} - 2e_{m,n} + e_{m+1,n} + e_{m-1,n+1} - 2e_{m,n+1} + \\
&\quad + e_{m+1,n+1}) - [f(n+1) + f(n)], \\
\frac{g_{m,n+1} - g_{m,n}}{\Delta t} &= \frac{D_g}{2\Delta x^2}(g_{m-1,n} - 2g_{m,n} + g_{m+1,n} + g_{m-1,n+1} - 2g_{m,n+1} + \\
&\quad + g_{m+1,n+1}) + \frac{1}{2}[f(n+1) + f(n)], \\
\frac{z_{m,n+1} - z_{m,n}}{\Delta t} &= \frac{D_z}{2\Delta x^2}(z_{m-1,n} - 2z_{m,n} + z_{m+1,n} + z_{m-1,n+1} - 2z_{m,n+1} + \\
&\quad + z_{m+1,n+1}) + \frac{1}{2}[f(n+1) + f(n)],
\end{aligned} \tag{7}$$

where:

$$f = k_1 e^2 - 4k_2 zg = F(e, g, z). \tag{8}$$

Taking into account the system of equations (7) the concentrations for the next interval of time for every point in film, are given by:

$$\begin{aligned}
\left(1+2\frac{D_e\Delta t}{2\Delta x^2}\right)e_{m,n+1} &= \frac{D_e\Delta t}{2\Delta x^2}(e_{m-1,n}+e_{m+1,n}+e_{m-1,n+1}+e_{m+1,n+1})+\\
&+\left(1-2\frac{D_e\Delta t}{2\Delta x^2}\right)e_{m,n}-\Delta t[f(n+1)+f(n)],\\
\left(1+2\frac{D_g\Delta t}{2\Delta x^2}\right)g_{m,n+1} &= \frac{D_g\Delta t}{2\Delta x^2}(g_{m-1,n}+g_{m+1,n}+g_{m-1,n+1}+g_{m+1,n+1})+\\
&+\left(1-2\frac{D_g\Delta t}{2\Delta x^2}\right)g_{m,n}+\frac{\Delta t}{2}[f(n+1)+f(n)],\\
\left(1+2\frac{D_z\Delta t}{2\Delta x^2}\right)z_{m,n+1} &= \frac{D_z\Delta t}{2\Delta x^2}(z_{m-1,n}+z_{m+1,n}+z_{m-1,n+1}+z_{m+1,n+1})+\\
&+\left(1-2\frac{D_z\Delta t}{2\Delta x^2}\right)z_{m,n}+\frac{\Delta t}{2}[f(n+1)+f(n)].
\end{aligned} \tag{9}$$

Using the following notations for the moduli of the three equations:

$$M_e = \frac{D_e\Delta t}{2\Delta x^2},\quad M_g = \frac{D_g\Delta t}{2\Delta x^2},\quad M_z = \frac{D_z\Delta t}{2\Delta x^2}, \tag{10}$$

and:

$$k_e = \frac{1}{1+2M_e},\quad k_g = \frac{1}{1+2M_g},\quad k_z = \frac{1}{1+2M_z}, \tag{11}$$

$$k_{pe} = 1-2M_e,\quad k_{pg} = 1-2M_g,\quad k_{pz} = 1-2M_z, \tag{12}$$

the system of finite differences equations (9) becomes:

$$\begin{aligned}
e_{m,n+1} &= k_e\{k_{pe}e_{m,n}+M_e(e_{m-1,n}+e_{m+1,n}+e_{m-1,n+1}+e_{m+1,n+1})-\\
&\quad-\Delta t[f(n+1)+f(n)]\},\\
g_{m,n+1} &= k_g\left\{k_{pg}g_{m,n}+M_g(g_{m-1,n}+g_{m+1,n}+g_{m-1,n+1}+g_{m+1,n+1})+\right.\\
&\quad\left.+\frac{\Delta t}{2}[f(n+1)+f(n)]\right\},\\
z_{m,n+1} &= k_z\left\{k_{pz}z_{m,n}+M_z(z_{m-1,n}+z_{m+1,n}+z_{m-1,n+1}+z_{m+1,n+1})+\right.\\
&\quad\left.+\frac{\Delta t}{2}[f(n+1)+f(n)]\right\}.
\end{aligned} \tag{13}$$

After the terms for actual time are ordered, one may obtain the following equations for the next time concentrations:

$$
\begin{aligned}
e_{m,n+1} &= r_{m,n} + k_e[M_e(e_{m-1,n+1} + e_{m+1,n+1}) - \Delta t f(n+1)], \\
g_{m,n+1} &= s_{m,n} + k_g\left[M_g(g_{m-1,n+1} + g_{m+1,n+1}) + \frac{\Delta t}{2} f(n+1)\right], \\
z_{m,n+1} &= t_{m,n} + k_z\left[M_z(z_{m-1,n+1} + z_{m+1,n+1}) + \frac{\Delta t}{2} f(n+1)\right],
\end{aligned} \tag{14}
$$

where $r_{m,n}$, $s_{m,n}$ and $t_{m,n}$ are concentration functions for E, G and Z molecular species at actual time or at level n.

The system of equations (14), which are nonlinear due to the nonlinearity of f function, has to be solved using an iterative method. For this purpose one may start by considering the values for e, g and z at the next time as being equals with those for the actual time, that is the initial ones, and to calculate e, g and z for $t = \Delta t$ (Δt being the time increment). In order to determine iteratively the values corresponding to $t = 2\Delta t$ one may consider as initial values those obtained by linear extrapolation of the values corresponding to $t = t_0$ and $t = t_0 + \Delta t$ (where t_0 is the initial time), that is:

$$
\begin{aligned}
e_{m,n+1} = 2e_{m,n} - e_{m,n-1}, \quad g_{m,n+1} = 2g_{m,n} - g_{m,n-1}, \\
z_{m,n+1} = 2z_{m,n} - z_{m,n-1}.
\end{aligned} \tag{15}
$$

For $t > 2\Delta t$ the initial values in iterative calculations may be obtained by parabolic extrapolation, as follows:

$$
\begin{aligned}
e_{m,n+1} = e_{m,n-2} + 3(e_{m,n} - e_{m,n-1}), \quad g_{m,n+1} = g_{m,n-2} + 3(g_{m,n} - g_{m,n-1}), \\
z_{m,n+1} = z_{m,n-2} + 3(z_{m,n} - z_{m,n-1}).
\end{aligned} \tag{16}
$$

For saving the computer memory only the results of previous two steps are recorded in the following matrices:

$$
\begin{aligned}
a(1,i) = e_{i,n-2}, \quad a(2,i) = e_{i,n-1}, \quad b(1,i) = g_{i,n-2}, \quad b(2,i) = g_{i,n-1}, \\
c(1,i) = z_{i,n-2}, \quad c(2,i) = z_{i,n-1}, \quad f(i) = F(e_{m,n+1}, g_{m,n+1}, z_{m,n+1}), \\
w(i) = F(e_{m,n}, g_{m,n}, z_{m,n}),
\end{aligned} \tag{17}
$$

where subscript i reffers to the position in film thickness, ($i = \overline{1, m+1}$).

It is necessary to actualize the equations (14) for initial and boundary conditions. So, for $t = t_0$, one has:

$$
\begin{aligned}
&n(i) = e_0, \quad v(i) = g_0, \quad x(i) = z_0, \quad f(i) = F(e_0, g_0, z_0) = w(i), \\
&a(1,i) = e_0, \; a(2,i) = e_0, \; b(1,i) = g_0, \; b(2,i) = g_0, \; c(i,1) = z_0, \; c(2,i) = z_0
\end{aligned} \tag{18}
$$

and for $t \neq t_0$:

$$
n(i) = e(i), \quad v(i) = g(i), \quad x(i) = z(i), \quad w(i) = F(e(i), g(i), z(i)). \tag{19}
$$

The functions e, g and z need only one subscript due to the fact that in the calculation procedure only the values for the last two time intervals and actual values are stored.

If boundary conditions (5) and (6) are considered one may obtain the following calculation formulas for the iterative process:

a) If $x = 0$ (that is $i = 1$), one has:

$$
\begin{aligned}
r(i) &= k_e[k_{pe}a(2,i) + 2M_e a(2,i) - \Delta t w(i)], \quad s(i) = g(i), \\
t(i) &= k_z \left[k_{pz} c(2,i) + 2M_z c(2,i) + \frac{\Delta t}{2} w(i) \right].
\end{aligned} \tag{20}
$$

b) If $x < x_0$, that is $i < m + 1$:

$$
\begin{aligned}
r(i) &= k_e\{k_{pe}a(2,i) + M_e[a(2,i-1) + a(2,i+1)] - \Delta t w(i)\}, \\
s(i) &= k_g \left\{ k_{pg} b(2,i) + M_g[b(2,i-1) + b(2,i+1)] + \frac{\Delta t}{2} w(i) \right\}, \\
t(i) &= k_z \left\{ k_{pz} c(2,i) + M_z[c(2,i-1) + c(2,i+1)] + \frac{\Delta t}{2} w(i) \right\}.
\end{aligned} \tag{21}
$$

c) If $x = x_0$ (that is $i = m + 1$):

$$
\begin{aligned}
r(i) &= k_e[k_{pe}a(2,i) + 2M_e a(2,i-1) - \Delta t w(i)], \\
s(i) &= k_g \left[k_{pg} b(2,i) + 2M_g b(2,i-1) + \frac{\Delta t}{2} w(i) \right], \\
t(i) &= k_z \left[k_{pz} c(2,i) + 2M_z c(2,i-1) + \frac{\Delta t}{2} w(i) \right].
\end{aligned} \tag{22}
$$

In equations (20) and (22) it was considered that $a(2, i-1) = a(2, i+1)$, and the same for b and c vectors. This means spatial derivatives equals to zero at film interfaces (with the exception for ethylene glycol, for $x = 0$). Finally, one can obtain the following relationships for iterative calculation:

a) For $x = 0$:

$$
\begin{aligned}
e(i) &= r(i) + 2M_e k_e n(i) - \Delta t k_e f(i), \quad g(i) = s(i), \\
z(i) &= t(i) + 2M_z k_z x(i) + \frac{\Delta t}{2} k_z f(i).
\end{aligned} \tag{23}
$$

b) For $x < x_0$:

$$
\begin{aligned}
e(i) &= r(i) + k_e\{M_e[n(i-1) + n(i+1)] - \Delta t f(i)\}, \\
g(i) &= s(i) + k_g \left\{ M_g[v(i-1) + v(i+1)] + \frac{\Delta t}{2} f(i) \right\}, \\
z(i) &= t(i) + k_z \left\{ M_z[x(i-1) + x(i+1)] + \frac{\Delta t}{2} f(i) \right\}.
\end{aligned} \tag{23'}
$$

c) For $x = x_0$:

$$
\begin{aligned}
e(i) &= r(i) + k_e[2M_e n(i-1) - \Delta t f(i)], \\
g(i) &= s(i) + k_g \left[2M_g v(i-1) + \frac{\Delta t}{2} f(i) \right], \\
z(i) &= t(i) + k_z \left[2M_z x(i-1) + \frac{\Delta t}{2} f(i) \right].
\end{aligned} \tag{23''}
$$

Iterative process ends when the following error conditions are simultaneously fulfilled:

$$
\mathrm{er}e < \mathrm{er}, \quad \mathrm{er}g < \mathrm{er}, \quad \mathrm{er}z < \mathrm{er}, \tag{24}
$$

where er is an imposed given error. The values of e, g and z errors are actualized after each iteration, using the relationships:

$$
\begin{aligned}
\mathrm{er}e &= \max\{|e(i) - n(i)|, \quad 1 \le i \le m+1\}, \\
\mathrm{er}g &= \max\{|g(i) - v(i)|, \quad 1 \le i \le m+1\}, \\
\mathrm{er}z &= \max\{|z(i) - x(i)|, \quad 1 \le i \le m+1\}.
\end{aligned} \tag{25}
$$

The mean values on film thickness for E, G and Z molecular species concentrations are calculated at the end of the iterative process using the trapezoidal rule, as follows:

$$
\begin{aligned}
s_e &= \frac{\int_0^{x_0} e\,dy}{\int_0^{x_0} dy} = \frac{\frac{\Delta x}{2}\{e(1)+2[e(2)+\ldots+e(i)]+e(i+1)\}}{x_0} = \\
&= \frac{1}{m}\left[\frac{e(1)}{2}+e(2)+\ldots+e(i)+\frac{e(i+1)}{2}\right], \\
s_g &= \frac{\int_0^{x_0} g\,dy}{\int_0^{x_0} dy} = \frac{\frac{\Delta x}{2}\{g(1)+2[g(2)+\ldots+g(i)]+g(i+1)\}}{x_0} = \\
&= \frac{1}{m}\left[\frac{g(1)}{2}+g(2)+\ldots+g(i)+\frac{g(i+1)}{2}\right], \\
s_z &= \frac{\int_0^{x_0} z\,dy}{\int_0^{x_0} dy} = \frac{\frac{\Delta x}{2}\{z(1)+2[z(2)+\ldots+z(i)]+z(i+1)\}}{x_0} = \\
&= \frac{1}{m}\left[\frac{z(1)}{2}+z(2)+\ldots+z(i)+\frac{z(i+1)}{2}\right].
\end{aligned} \tag{26}
$$

Finally, one may calculate the polycondensation degree:

$$\overline{\mathrm{PD}} = \frac{1}{1-x_e}, \tag{27}$$

where x_e is E molecular species conversion.

Substituing the values calculated earlier, one may obtain:

$$\overline{\mathrm{PD}} = \frac{1}{1-(1-s_e/e_0)} = \frac{e_0}{s_e}. \tag{28}$$

Using the above algorithm a computer program in PASCAL was developed. Program parameters were established as follows:

1. The diffusion coefficient for ethylene glycol, D_g, was approximated to the lower limit, $D_g \geq 1.6 \times 10^{-8}$ m^2/s [6].

2. The diffusion coefficients for bis(2-hydroxyethylterephtalate) and poly(ethyleneterephtalate) melt were arbitrarily taken as function of that of ethylene glycol.

3. Initial concentration for bis(2-hydroxyethylterephtalate) was 5 mole/l, for ethylene glycol 0.5 mole/l and for the polymer 0.1 mole/l.

4. The concentration of the ethylene glycol at the film interface, g_i, and film thickness, x_0, were considered variables.

5. Reaction rate constant $k_1 = 1.8 \times 10^{-3}$ l/mole.sec. [2] and k_2 was varied so that the equilibrium constant $K = k_1/k_2$ to be situated in the domain 1...100.

4. Discussions

Fig. 1 shows the variation of polycondensation degree versus time for different values for the equilibrium constant K.

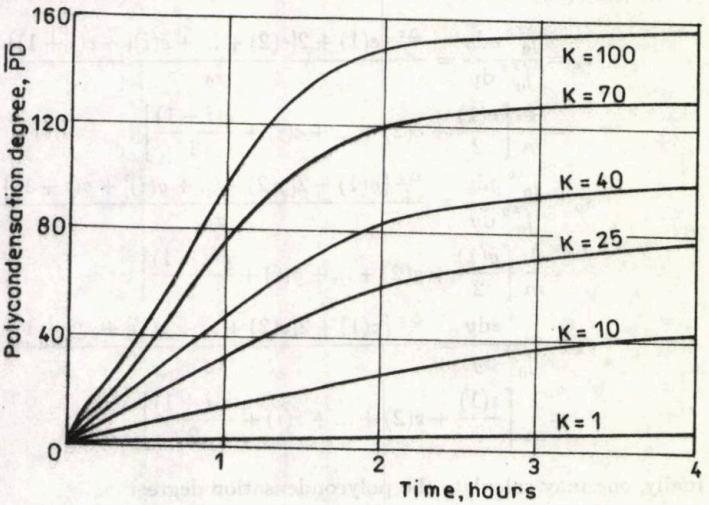

Fig. 1.– Variation of polycondensation degree with time for different values of the equilibrium constant K, ($D_g/D_e = 10$; $D_z/D_e = 10^{-1}$; $g_i = 10^{-2}$ mole/l; $x_0 = 10^{-3}$ m).

It may be noticed that, in every case, the process undergoes in such a manner that a limit is asymptotically reached for PD, which is a function of K value. One may obtain values of about 100 for the polycondensation degree if $K = 40$ and at reaction time between three and four hours, close to industrial process time. For this reason, in the next runs of the program we considered $K = 40$ and variable values for the rest of the parameters. As expected, the higher K value is, the higher the polycondensation degree will be.

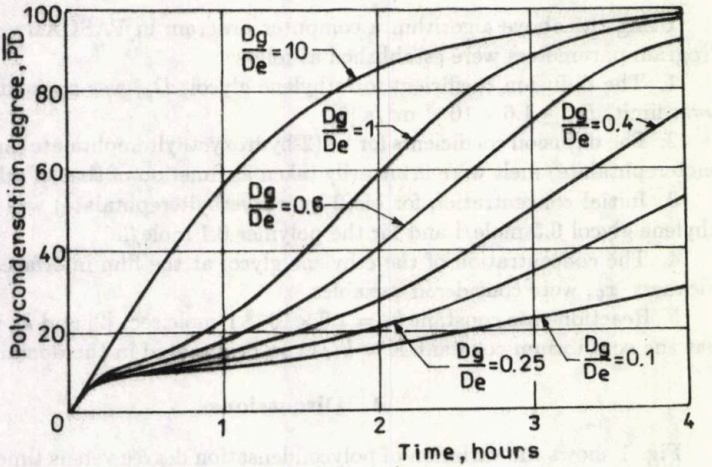

Fig. 2.– The influence of the diffusion coefficient of the ethylene glycol (D_g) on the polycondensation degree ($D_z/D_e = 10^{-3}$; $g_i = 10^{-2}$ mole/l; $K = 40$; $x_0 = 10^{-3}$ m).

References are very poor for the diffusion coefficients of micromolecular liquids

in polymeric melts, so that in Fig. 2 the influence of the variation of diffusion coefficient for ethylene glycol is represented.

It may be noticed that final polycondensation degree increases when D_g/D_e ratio increases too and one may conclude that ethylene glycol diffusion is about ten times faster than that of bis(2-hydroxyethyl)terephtalate. In all cases it was considered that $D_z/D_e = 10^{-3}$. The results are about the same even if the ratio D_z/D_e is one hundred time higher, showing a minor influence of the mobility of polymer molecules, due to its reduced value.

An interesting aspect of the polycondensation process is that of the influence of the vacuum, which enhances the transfer of ethylene glycol molecules to the film interface. This may be studied by taking into account different values for ethylene glycol concentration at melt film interface. In Fig. 3 are presented the curves of variation of polycondensation degree against time for various ethylene glycol concentrations at film interface comprised between 0 and 5×10^{-2} mole/l. It is seen that at high vacuum the variation of the polycondensation degree is almost linear with time. At moderate values of the vacuum, the polycondensation degree obtained after four hours is situated between 100 and 200. Fig. 3 shows, also, that under high pressure proper values for polycondensation degree can't be obtained even if the reaction time is long enough.

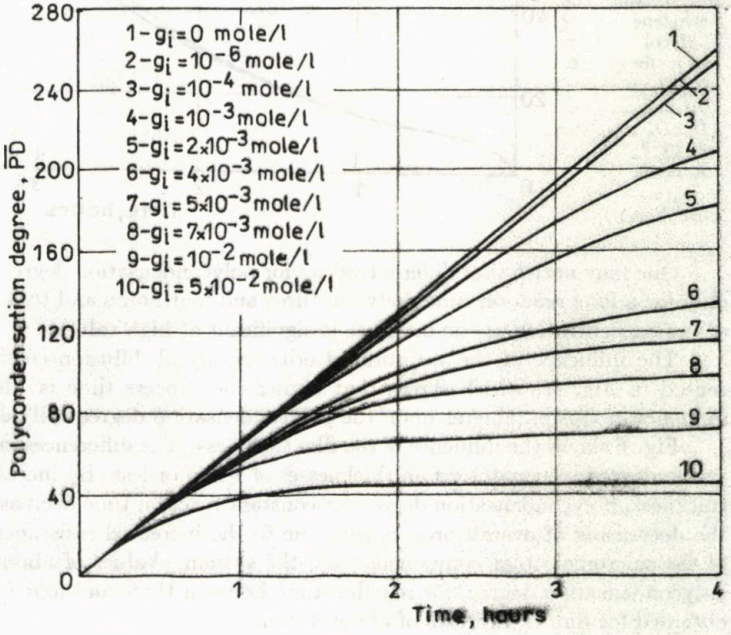

Fig. 3.– Variation of polycondensation degree with time for different values of the interface concentration of the ethylene glycol (g_i), for $D_g/D_e = 10$, ($D_z/D_e = 10^{-3}$; $K = 40$; $x_0 = 10^{-3}$ m).

The influence of ethylene glycol concentration at film interface depends, also,

on the diffusion coefficients of the others components as it's shown in Fig. 4, where a D_g/D_e ratio of 0.4 was considered as compared with 10, for the conditions in Fig. 3.

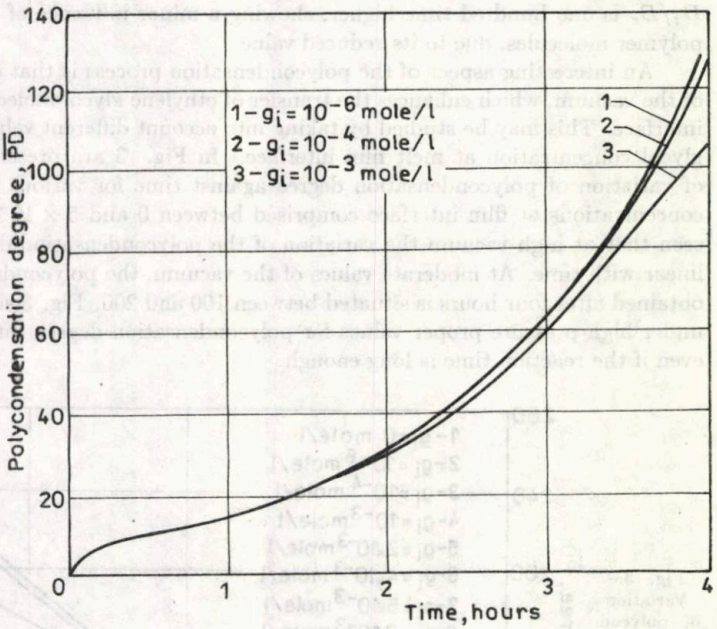

Fig. 4.– Variation of polycondensation degree with time for different values of the interface concentration of the ethylene glycol (g_i), for $D_g/D_e = 0.4$, ($D_z/D_e = 10^{-3}$; $K = 40$; $x_0 = 10^{-3}$ m).

One may notice that different values for polycondensation degree are obtained only for a long reaction time, between three and four hours and that the influence of the concentration at the interface is significant at high values.

The influence of the variation of ethylene glycol diffusion coefficient is presented in Fig. 5, which shows that higher the process time is, the higher the influence of this parameter upon the polycondensation degree will be.

Fig. 6 shows the influence of the film thickness. The differences in polycondensation degree are small for film thicknesses of 1 mm or less. By increasing the film thickness, polycondensation degree for constant reaction time decreases because of the decreasing of overall process rate due to the increased resistance to diffusion of the micromolecular component from the system. Values of about 100 for the polycondensation degree, for reaction time between three and four hours, may be obtained for film thicknesses of about 3 mm.

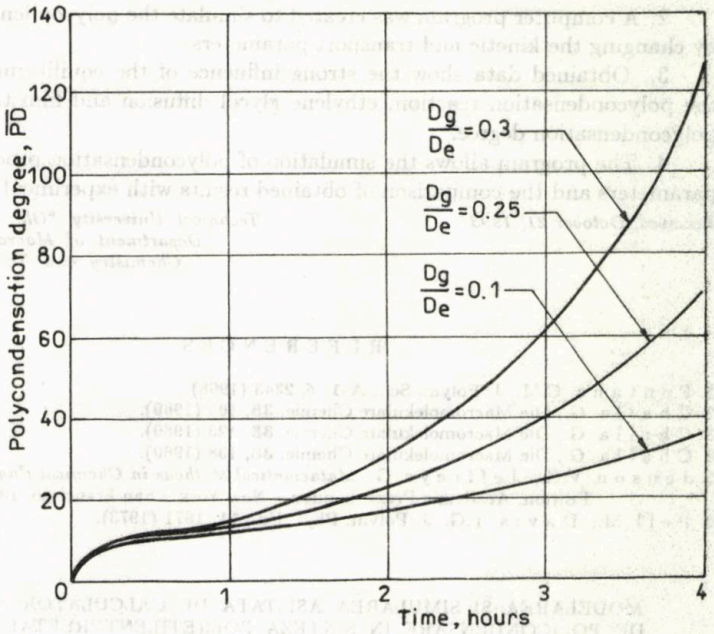

Fig. 5.– The influence of the diffusion coefficient of the ethylene glycol (D_g) on the polycondensation degree ($D_z/D_e = 10^{-3}$; $g_i = 10^{-6}$ mole/l; $K = 40$; $x_0 = 10^{-3}$ m).

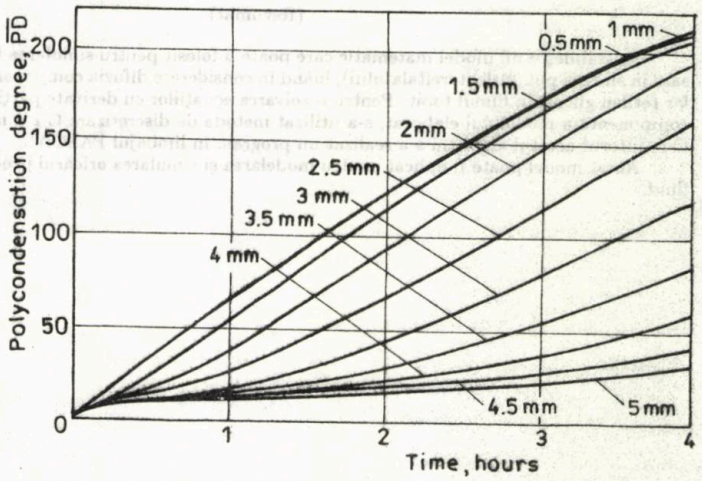

Fig. 6.– Effect of time and film thickness on the polycondensation degree ($D_g/D_e = 10$; $D_z/D_e = 10^{-3}$; $g_i = 10^{-3}$; $K = 40$).

5. Conclusions

1. A mathematical model was developed for film polycondensation process of bis(2-hydroxyethyl)terephthalate in the synthesis of poly(ethyleneterephthalate), taking into account the diffusion of micromolecular component (ethylene glycol).

2. A computer program was created to simulate the polycondensation process by changing the kinetic and transport parameters.

3. Obtained data show the strong influence of the equilibrium constant of the polycondensation reaction, ethylene glycol diffusion and film thickness upon polycondensation degree.

4. The program allows the simulation of polycondensation process for sets of parameters and the comparison of obtained results with experimental data.

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MODELAREA ŞI SIMULAREA ASISTATĂ DE CALCULATOR A FAZEI DE POLICONDENSARE ÎN SINTEZA POLI(ETILENTEREFTALATULUI)

(Rezumat)

Se stabileşte un model matematic care poate fi folosit pentru simularea fazei de policondensare în sinteza poli(etilentereftalatului), luând în considerare difuzia componentului micromolecular (etilen glicol) în filmul topit. Pentru rezolvarea ecuaţiilor cu derivate parţiale, care sunt parte componentă a modelului elaborat, s-a utilizat metoda de discretizare Crank-Nicolson. Cu ajutorul acestui algoritm s-a realizat un program în limbajul PASCAL.

Acest model poate fi aplicat pentru modelarea şi simularea oricărui proces heterogen fluid–fluid.

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CHIMIE ŞI INGINERIE CHIMICĂ

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MECHANO-CHEMICALLY INITIATED POLYMERIZATIONS
THE MEDIUM NATURE INFLUENCE ON THE POLYMERIZATION OF ACRYLAMIDE BY VIBRATORY MILLING

BY
CLEOPATRA VASILIU-OPREA and JEANA NICOLEANU

1. Introduction

It is generally known that the kinetic energy released by vibratory milling is used, at least partially, for the excitation of the superficial layers of the building material of the apparatus (the vessel's walls and the milling bodies), inducing elimination of some electronic fluxes whose velocity and efficiency depend, on one side, on the amount of kinetic energy released and, on the other, on the nature of the fluid medium constituting the gaseous atmosphere within which the polymerization reaction is developed [1],...,[9].

The paper deals with the influence of the medium's nature on the mechano-chemical polymerization of acrylamide, for clearing up its reaction mechanism. The emission of the electronic fluxes through vibratory nilling, during acrylamide polymerization, was indirectly emphasized by the modification of the inert atmosphere inside the reaction vessel.

As a matter of fact, the intensity and velocity of the mechano-emission fluxes are influenced by the nature of the media they penetrate, more precisely, by the molecular size of their constituents. To this end, a series of experiments using N_2, Ar and CO_2 as gaseous atmosphere was performed, the results being compared with those obtained in vacuum (10^{-4} mm Hg).

2. Experimental

2.1. Equipment, Materials and Methods

The experiments were performed on a LS-60 Labowi type vibratory mill. The reaction vessels were made of V2A stainless steel, having a 800 mL capacity and cylindrical form, the threaded lid being equipped with valves. The reaction vessels were thermostated by means of four reaction vessels, mounted in a thermostating casing equipped with connecting pipes, for the recirculation of the cooling water.

300 g of grinding bodies made of V2A stainless steel, 3.00 mm in diameter, were used, at a filling ratio of 0.30%.

The reaction vessels were introduced in a trap filled with liquid nitrogen, then vacuum was applied (10^{-4} mm Hg). Three vessels were filled with N_2, Ar and CO_2, while the fourth was kept under vacuum.

Acrylamide of analytical reagent-grade was additionally purified by recrystallization from benzene and then vacuum-dried. Purification of polyacrylamide and the experimental techniques were previously discussed [6], [7].

2.2. Influence of the Gaseous Medium on the Conversion Degree

Variation of conversion with the reaction time has been investigated in three-chemically inert *versus* the reaction system – gaseous media, namely N_2, Ar and CO_2, constituted of molecules with variable dimensions. The obtained experimental results were compared to those acquired in high vacuum (10^{-4} mm Hg).

It was noticed that the smaller size of the constituent molecules of the employed gas, the smaller was the inhibiting effect of the mechano-emission flux thus induced, which led to higher conversion degrees. The highest values of the conversion degrees are obtained in vacuum (Fig. 1, curve *1*).

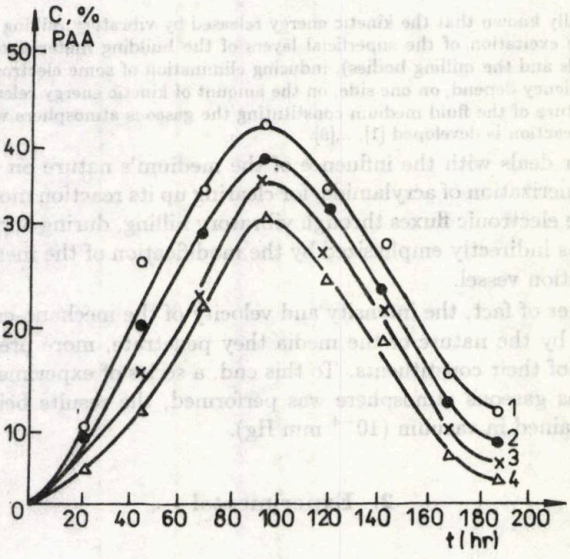


Fig. 1.– Conversion – time curves of the mechano-chemical polymerization of acrylamide using various gaseous media: *1* – vacuum; *2* – nitrogen; *3* – argon; *4* – carbon dioxide.

The bigger the sizes of the gas molecules (in our case, the order being vacuum, nitrogen, argon, carbon dioxide), the stronger was the induced effect of inhibition

on the mechano-emission electronic fluxes. A direct relationship is thus established between the molecular size of the gaseous medium and the obtained value for the conversion degree, which evidences the role played by the mechano-emission electronic flux initiating polymerization of the monomer subjected to investigation.

2.3. Influence of some Radical Acceptors on the Conversion Degree

In order to establish the nature of the active centers involved in mechano-chemical polymerization, the experiments were performed in the presence of some radical acceptors (such as phenol and hydroquinone) in amounts of about 1.0% *versus* the monomer.

The influence of the radical acceptors on the conversion degree is quite strong, as seen in Fig. 2; mention is to be made here of hydroquinone's stronger influence (curve *3*), as compared with phenol (curve *2*).

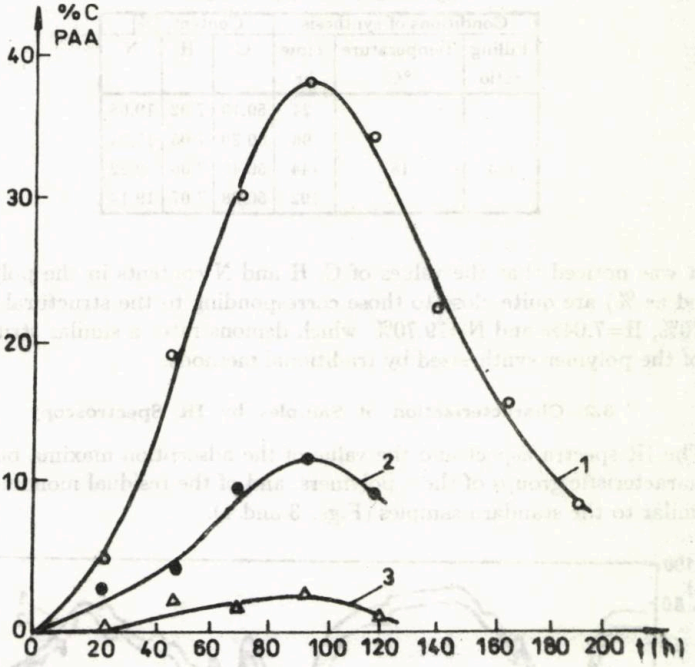


Fig. 2.– Conversion – time curves of the mechano-chemical polymerization of acrylamide: *1* – without inhibitor; *2* – phenol; *3* – hydroquinone.

Thus, in the absence of inhibitors, on maintaining the other parameters unchanged, the maximum degree of conversion attained is of 42.0%, while in the presence of phenol it decreases to 12.25% and to 2.25%, respectively, in the presence of hydroquinone.

The maximum value of the conversion degree is recorded again for a duration of the polymerization reaction of 96 hours. The obtained data are in good agreement with the previous ones [6].

3. Characterization of the Reaction Products

3.1. Determination of Chemical Composition by Elemental Analysis

Results of the elemental analysis of the polyacrylamide samples synthesized mechano-chemically, under various reaction conditions, are shown in Table 1.

Table 1
Elemental Analysis of Polyacrylamide Synthesized in High Vacuum

Conditions of synthesis			Content, [%]		
Filling ratio	Temperature °C	Time hr	C	H	N
0.3	18	24	50.10	7.02	19.08
		96	50.30	7.05	19.24
		144	50.40	7.06	19.22
		192	50.38	7.07	19.14

It was noticed that the values of C, H and N contents in the polymers (expressed as %) are quite close to those corresponding to the structural unit: C = =50.70%; H=7.04% and N=19.70%, which demonstrates a similar structure with that of the polymer synthesized by traditional methods.

3.2. Characterization of Samples by IR Spectroscopy

The IR spectra aspect and the value of the adsorption maxima belonging to the characteristic groups of these polymers, and of the residual monomer, as well, are similar to the standard samples (Figs. 3 and 4).

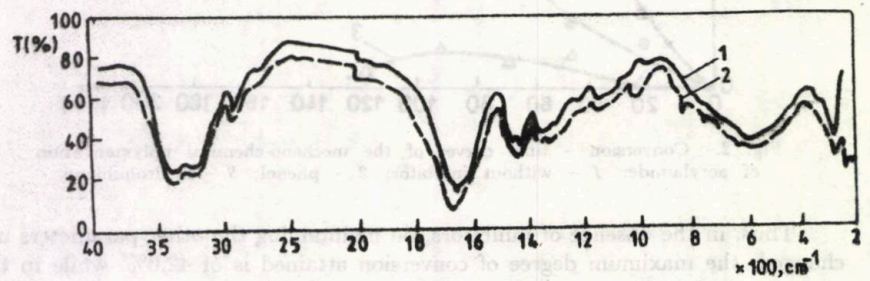


Fig. 3.– IR spectra of polyacrylamide: *1* – polyacrylamide synthesized mechano-chemically, *2* – polyacrylamide synthesized by classical methods.

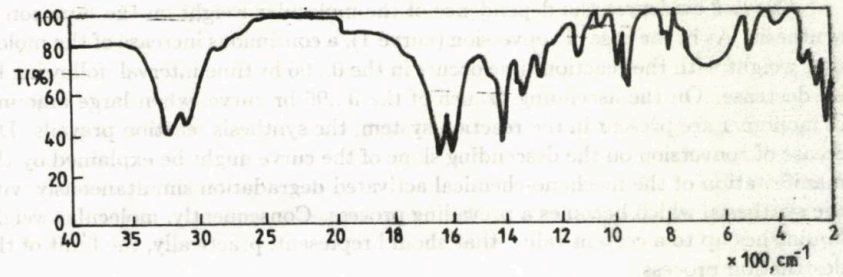


Fig. 4.– IR spectra of acrylamide.

A slight shifting of some bands within the lower wave lenght domain (from 1 435 cm to 1 310 cm) may be noticed or, in other cases, a slight broadening of the corresponding peaks (for instance, 3 325 cm), as a consequence of the existence of supertensioned bonds on the macromolecular chain.

3.3. Molecular Weight Determination

The molecular weight was measured viscosimetrically. The applied technique and the obtained equation have been discussed in previous papers [6], [7]. The experimental results are presented in Fig. 5.

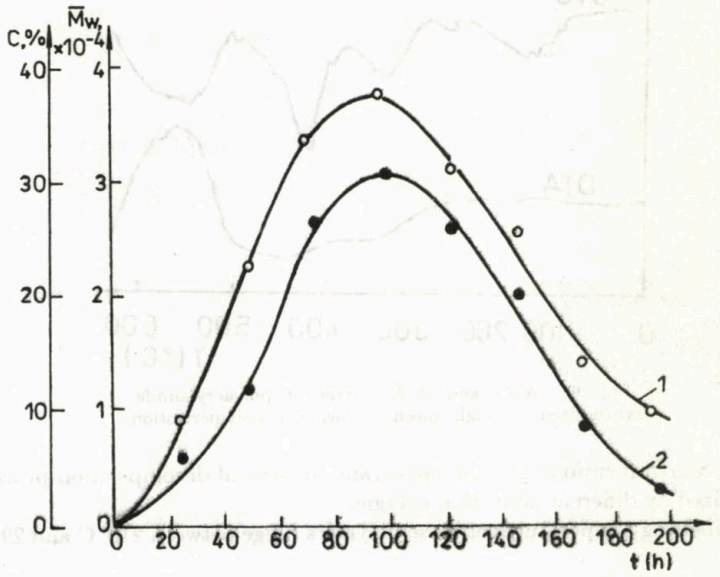


Fig. 5.– Influence of grinding duration on the conversion degree (*1*) and molecular weight (*2*).

Curve *2* evidences the dependence of the molecular weight on the duration of synthesis. As in the case of conversion (curve *1*), a continuous increase of the molecular weight with the reaction time occurs in the 0...96 hr time interval, following by its decrease. On the ascending branch of the 0...96 hr curve, when large amounts of monomer are present in the reaction system, the synthesis reaction prevails. Decrease of conversion on the descending slope of the curve might be explained by the manifestation of the mechano-chemical activated degradation simultaneously with the synthesis, which becomes a prevailing process. Consequently, molecular weight diminishes up to a certain value, that should represent, practically, the limit of the destruction process.

3.4. Polymer Characterization by X-ray Diffraction

X-ray diffraction spectra characterize the products obtained as amorphous substances resulted by the destruction of the monomer's crystalline network, polymerization occurring on the surfaces continuously renewed through vibratory milling.

3.5. Thermostability

Thermogravimetric and thermodifferential curves plotted in Figs. 6 and 7 show that the polyacrylamide presents good thermostability; at 200°C it losses maximum 15.0% of its weight.

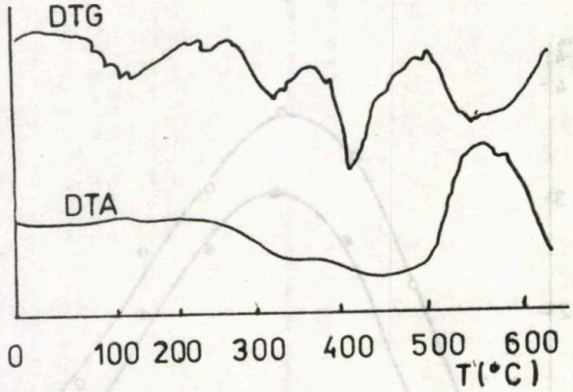


Fig. 6.– ATG and ATD curves of polyacrylamide synthesized through mechano-chemical polymerization.

Also, worth mentioning is the appearance of several decomposition processes characterized by different activation energies.

The melting temperatures of these polymers range between 210°C and 293°C.

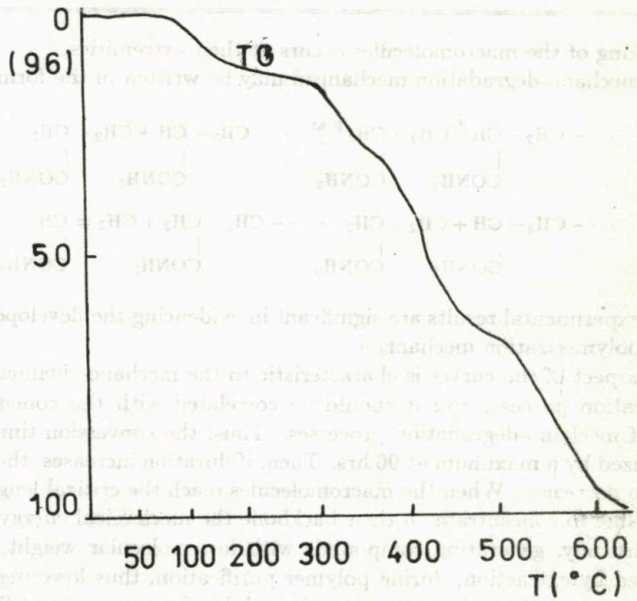


Fig. 7.– Variation of losses of polyacrylamide synthesized through mechano-chemical polymerization.

4. Results and Discussion

Correlation of the experimental results in the study of the mechano-chemical synthesis on the nature of the active and inert media leads to the conclusion that the mechano-emission of electronic fluxes induces the appearance of primary active centers, of the anion-radicalic type:

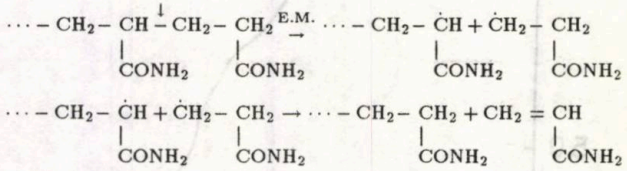
$$CH_2 = \underset{\underset{CONH_2}{|}}{CH} + e^- \rightarrow \left[\ddot{C}H_2 - \underset{\underset{CONH_2}{|}}{\dot{C}H} \leftrightarrow \dot{C}H_2 - \underset{\underset{CONH_2}{|}}{\ddot{C}H} \right]$$

Lowering of conversions in the presence of active media, of the acceptor type, demonstrates their subsequent evolution by a radicalic mechanism of polymerization.

The obtained experimental data, plotted as time – conversion curves, evidence the occurrence of mechano-degradation simultaneously with the synthesis; the macromolecules having exceeded the critical length become capable to accumulate mechanical energy; when the adsorbed energy becomes at least equal to that of the chemical bond, its homolytical split takes place; by mechano-degradation, the molecular weight decreases. Also, increase of the polymer's solubility in acetone – a specific solvent for the monomer – was experimentally observed, which proves

that breaking of the macromolecules occurs at their extremities.

The mechano-degradation mechanism may be written in the form:



The experimental results are significant in evidencing the developement of the radicalic polymerization mechanism.

The aspect of the curves is characteristic to the mechano-chemically initiated polymerization process, and it should be correlated with the concurrent development of mechano-degradation processes. Thus, the conversion-time curves are characterized by a maximum at 96 hrs. Then, if duration increases, the duration of conversion decreases. When the macromolecules reach the critical length, they become capable to concentrate on their backbone the mechanical energy, they break up homolitically, generating compounds with low molecular weight, which may be removed by extraction, during polymer purification, thus lowering conversion. As in the case of the polyacrylamide, the soluble fraction is identified with the monomer; there results that mechano-degradation takes place at the extremities of the macromolecular chain.

5. Conclusions

1. Mechano-emission of electronic fluxes generates primary active centers of the anion-radicalic type, for the mechano-chemical polymerization of acrylamide in solid state. Their intensity is determined by the size of the molecules forming the gaseous atmosphere in the reactor in which the polymerization reaction takes place.

2. Polymerization develops according to a concatenation radicalic mechanism in the superficial layers, mechanically destroyed, of the monomers' crystalline network.

3. The mechano-chemically synthesized polyacrylamide – due to its physico-chemical properties – presents a good analogy with the polymer obtained by other methods.

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POLIMERIZĂRI INIŢIATE MECANO-CHIMIC

Influenţa naturii mediului asupra polimerizării acrilamidei prin măcinare vibratorie

(Rezumat)

Se studiază influenţa naturii mediului asupra polimerizării mecano-chimice a acrilamidei, în vederea elucidării mecanismului de reacţie. Se dovedeşte capacitatea fluxurilor electronice de mecano-emisie de a genera centrele active primare, de tip anion-radicalice, ale polimerizării monomerului în stare solidă. Produsele de reacţie se caracterizează prin metode fizice şi chimice (analiză elementară, spectroscopie IR, termogravimetrie, determinarea masei moleculare, difracţia cu raze X etc.).

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MECHANO-CHEMICAL DEGRADATION OF POLYETHYLENETEREPHTHALATE STABILIZED WITH EPOXIDE DURING SHEARING THROUGH CAPILLARIES

BY

CLEOPATRA VASILIU-OPREA and AL. SAVIN

1. Introduction

In processes of polyethyleneterephthalate (PET) melt shearing through capillaries, thermo-mechanical degradation occurs, resulting in the modification of the polymer properties.

A direct consequence of the degradation phenomenon is the splitting of the polyester chain, especially at the ends of these ones, which induces lowering of the molecular weight and also formation of new final carboxylic groups. The increase of the concentration of the final carboxylic groups in the polyester intensifies degradation [1].

A reduced content of carboxylic groups is significant for the thermal and hydrolytic stability of the products obtained by PET melts extrusion [1].

Lowering of the effects of thermo-mechanical degradation may be achieved by selecting the optimal geometry of the flow direction for the PET melt and also by the utilization of carboxylic groups inhibitors.

In recent years, most of the researchers suggest the utilization of epoxides for blocking the carboxylic groups from PET, even if trialkyl- or triaryl-phosphates and the corresponding esters of the thiophosphoric acid have been the first stabilizers of the PET melts [2].

Also, the introduction of epoxides in PET, both in the polycondensation [3], [4] and in the spinning stage [5], [6], is proposed. Several patents have to be mentioned, discussing various procedures for the obtainment of PET with a low content of carboxylic groups, by the utilization of phenyl-glycidyl-ether (PGE), [5], [6], and N-glycidyl-phthalimide, [4], [7], [8], as inhibitors.

Nevertheless, few studies are to be found in literature, devoted to the utilization of epoxides for lowering the concentration of the carboxylic groups from PET [10], [11].

In the present paper the influence of the epoxide as well as of the way it is introduced into the polymer, upon certain characteristics of the product resulted after shearing of the PET melt through capillaries is analyzed.

The stabilizers effect has been expressed as a function of the properties including inherent viscosity and concentration of the final carboxylic groups.

2. Experimental

2.1. Materials

PET granules, with an initial inherent viscosity of 0.820 dL/g and a content of 18 equiv. COOH/t.

Phenyl-glycidyl-ether (PGE) synthesized by the method usually recommended in literature [12], having $n_D^{20} = 1.5302$, $d_{20} = 1.108$ g/cm^3, $t_b/17$ mm Hg =

= 129°...130°C and epoxidic equivalent = 153.

2.2. Equipment

An Instron rheometer, Model 3212, equipped with a wolfram carbide capillary, 1 mm in diameter, L/D ratio = 67 and entering angle of 90°, has been employed.

2.3. Experimental Method

Experimental determinations employed PET granules treated with epoxide, according to the following procedures:

a) Application of the epoxide on the granules surface. Consequently the PET granules, dried in vacuum at a temperature of 130°C, have been introduced, together with a certain amount of epoxide in a closed vial, and stirred in order to obtain an as much as uniform possible distribution on the surface.

b) Introduction of the epoxide into the polymer's mass. PGE was introduced in the PET melt prior to the termination of the polycondensation reaction; the mixture was then stirred for 15 min.

The granules obtained after extrusion of this melt have been vacuum-dried, at a temperature of 130°C, being then introduced into the rheometer's reservoir.

For comparison, granules without epoxides, vacuum-dried at a certain temperature, have been also employed.

The utilized amount of epoxide represented 0.5% of the weight of the polymer introduced for stabilization.

In order to eliminate thermooxidative processes, the introduction of the PET granules into the rheometer was performed under nitrogen.

At extrusion temperatures of 270°, 290°, 310°C, shearing rates of 45; 150; 450; 1 500 sec^{-1} have been used.

2.4. Quantitative Analysis

The viscosities of PET solutions has been measured on an Ubbelohde viscosimeter, on employing a phenol/1,1,2,2-tetrachloroethan (60/40 g/g) solvent mixture, at 25°±0.01°C. The concentrations of the PET solutions were of 0.5 g/dL. At least three determinations have been performed for each sample.

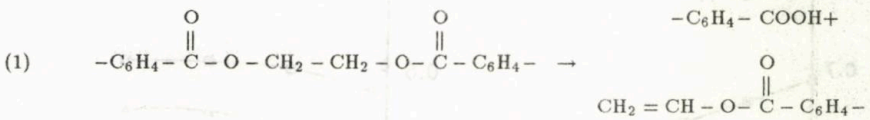
Determinations of the final carboxylic groups was performed by acidimetric titrations, in a benzylic alcohol–chlorophorm mixture, at 60°C. Alkaline solutions of NaOH 0.1 N in benzylic alcohol and a solution of red-phenol, as indicator, have been used.

3. Results and Discussion

During the extrusion of the PET melts through the capillaries, under the combined action of thermal and mechanical energy, macromolecules are subjected to deformations, chains scissions, reticulation.

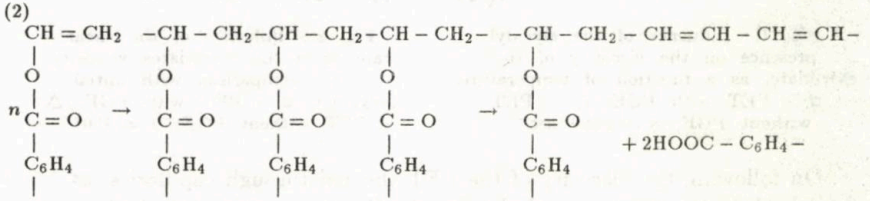
Scission of the PET chain occurs statistically, new final groups and shorter chains being thus obtained [13].

Usually, scissions occur at esteric links, generating a carboxyl group at each scission:



Nevertheless, PET's thermal degradation is manifested not only by chain breaking but also by their reticulation or of the fragments formed through scission.

The final vinyl–ester groups may participate in polymerization reactions, thus generating branched structures which, in their turn, may eliminate smaller chain fragments:



This represents another modality for the formation of final carboxylic groups [14].

When mechanical energy intervenes in the process of extrusion through the capillaries, the effect of the thermal degradation is modified by viscous heating.

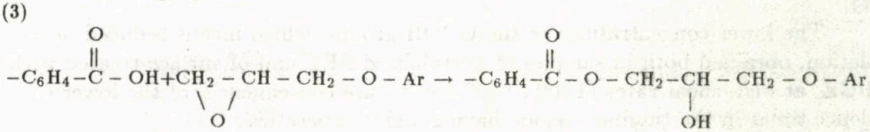
At low stationary times, corresponding to high shear rates, the heat evolved through viscous heating, at the capillary's wall, does not have the necessary time to be dissipated into the extrudate.

Consequently, the total degradation of the extruded polyester will be lower, at high shear rates.

On increasing the temperature and the stationary time in the shear forces field PET's degradation degree increases.

On the whole, the extruded pet will have a higher concentration in final carboxylic groups and a lower viscosity, as compared with the initial product.

In the presence of glycidyls, the concentration of the carboxylic groups from the extruded PET will be lowered, as a consequence of their blocking, according to the following equation:



The degradation processes will be inhibited. Consequently, the characteristics of the extruded PET will be improved.

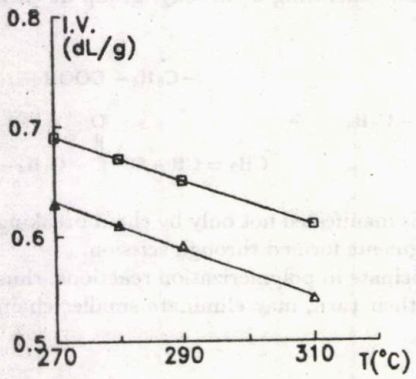


Fig. 1.– Influence of the glycidyl presence on the viscosity of the extrudate, as a function of temperature: □ – PET with PGE, △ – PET without PGE; $\dot{\gamma} = 1\,500$ sec^{-1}.

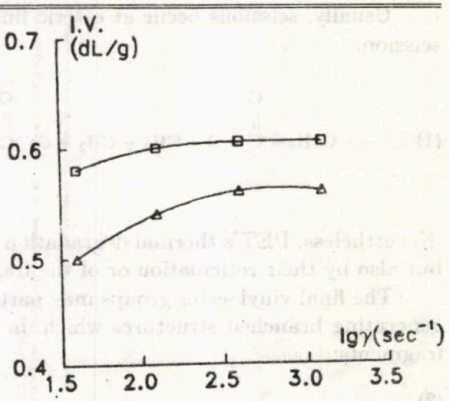


Fig. 2.– Influence of the shear rate upon the extrudates viscosity (in comparison with initial polymer): □ – PET with PGE, △ – PET without PGE; $T = 290°C$.

On following the viscosity of the PET sheared through capillaries, at 1 500 sec^{-1}, both in the presence and absence of PGE, one may observe higher values when employing glycidyle, on the whole temperature range (Fig. 1).

Higher viscosity values of the extruded obtained from PET stabilized with PGE, as compared with those of the untreated PET, have been obtained for all shear rates applied (Fig. 2).

Lower viscosities, obtained both for PGE-treated and untreated PET, at low shear rates, are explained by the higher residence times in the extrusion zone, at higher temperatures, as compared with the case of high shear rates application.

The epoxide's action may be followed, too, by the evolution of the concentration of the final carboxylic groups in the extruded polymer.

When employing PGE, the concentration of the COOH groups in the extruded PET is lower than in the case of nonstabilized PET, on increasing the temperature from 270°to 310°C (Fig. 3). Such behaviour agrees with the epoxides' mechanism of action, expressed by equation (3).

In the shear rate range considered, lowering of the COOH groups concentration was observed, in the extrudate obtained from PET stabilized with epoxides (Fig. 4).

The lower concentrations of the COOH groups, which means reduced degradation, obtained both in samples of unstabilized PET and of surface-treated with PGE, at high shear rates (1 200...1 500 sec^{-1}), are consequences of the lower residence times in the capillary region having high temperatures.

In a series of experiments we studied the influence of the way in which the inhibitor is introduced into the polymer upon the characteristics of the PET resulted from shearing through the capillary.

The introduction of PGE in the PET melt produces a polymer which, through

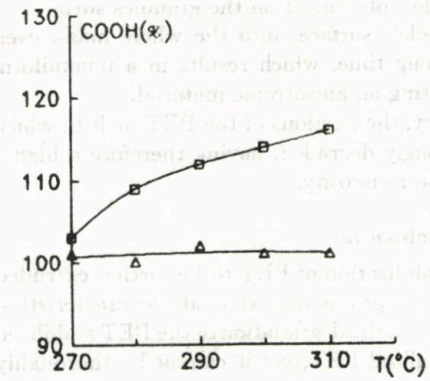


Fig. 3.– Dependence of COOH groups concentration in the extruded PET vs. the extrusion temperature (% in comparison with initial polymer): □ – untreated PET, △ – PGE surface treated PET; $\dot{\gamma} = 1500$ sec^{-1}.

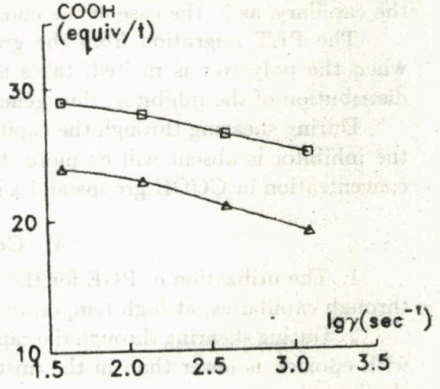


Fig. 4.– Influence of the shear rate on the concentration of the COOH groups in the extruded PET: □ – untreated PET, △ – PGE surface treated PET, $T = 290°C$.

shearing, is less degraded, as compared with the PET stabilized by the application of PGE on the granules surface.

The technique of PGE introduction into the PET influences, too, the process of COOH groups blocking, during extrusion through the capillary (Figs. 5 and 6).

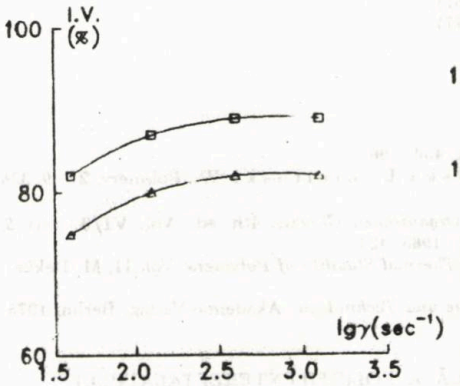


Fig. 5.– Influence of the shear rate on the viscosity of the extruded PET (% in comparison with initial polymer); □ – PGE mass stabilized PET; △ – PGE surface stabilized PET; $T = 290°C$.

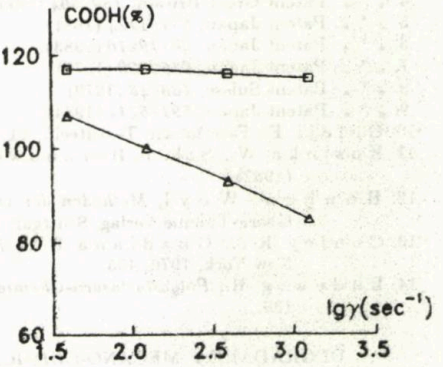


Fig. 6.– Influence of the shear rate on the concentration of the COOH groups in the sheared PET (% in comparison with the initial polymer): △ – PGE mass stabilized PET; □ – PGE surface stabilized PET; $T = 290°C$.

The distribution of PGE into the mass of polyester melt makes the blocking reaction of the carboxylic groups to be more rapid during the extrusion through

the capillary, as in the case of the epoxide's placement on the granules surface.

The PET migration from the granule's surface, into the whole mass, even when the polyester is melted, takes a long time, which results in a nonuniform distribution of the inhibitor, thus generating an anisotropic material.

During shearing through the capillary, the portions of the PET melt in which the inhibitor is absent will be more strongly degraded, having therefore a higher concentration in COOH groups and a lower viscosity.

4. Conclusions

1. The utilization of PGE for the stabilization of PET to be further extruded through capillaries, at high temperatures, improves the extrudates'characteristics.

2. During shearing through the capillary, the degradation of the PET stabilized with epoxide is lower than in the unstabilized PET, yet it cannot be thoroughly eliminated.

3. PET stabilization through the introduction of epoxide into the melt is more efficient than the treatment with epoxide only on the surface of the granules to be afterwards extruded at high temperatures.

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DEGRADAREA MECANO-CHIMICĂ A POLIETILENTEREFTALATULUI STABILIZAT CU EPOXID, ÎN TIMPUL FORFECĂRII PRIN CAPILARE

(Rezumat)

S-a studiat influenţa temperaturii (270°...310°C), a vitezei de forfecare (45...1 500 sec^{-1}) şi a modului de introducere a epoxidului în polimer asupra viscozităţii şi concentraţiei grupelor carboxilice finale din polimerul extrus prin capilare. La utilizarea fenil-glicidil-eterului s-au constatat diminuări ale proceselor de degradare, reflectate în micşorarea concentraţiei grupelor carboxilice finale şi scăderi mai mici ale viscozităţii inerente pentru polimerul extrus.

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RECENZII — BOOK REVIEWS

BARTZ W.J., (Federführend), *Additive für Schmierstoffe*. Expert Verlag, Fachverlag für Wirtschaft & Technik, Renningen, 1994, 457 S., ISBN 3-8169-0916-7.

Den meisten Schmier- und Kraftstoffen werden Wirkstoffe oder Additive zugesetzt, um bestimmte erwünschte Eigenschaften zu erzeugen und zu verstäken oder um bestimmte unerwünschte Eigenschaften zu unterdrücken oder abzuschwächen. Die Additive und ihre Konzentration sind dabei nicht nur auf die Grundflüssigkeit und den Anwendungsfall abzustimmen, vielmehr sind im Falle der Schmierstoffadditive auch die Wechselbeziehungen mit der Reibstelle zu berücksichtigen.

Im vorliegenden Buch werden die wichtigsten Additive beschrieben, welche die physikalischen, chemischen und physikalisch-chemischen Eigenschaften der Schmierstoffe verändern. Somit werden die folgenden Additivtypen behandelt: a) Oxidations- und Korrosionsinhibitoren; b) Aschegebende und aschefreie Extreme-Presure- und Verschleißschutzadditive; c) Festschmierstoffe; d) Friction Modifier; e) Detergent–Dispersant Additive; f) Viskozitätsindex-Verbesserer; g) Pourpoint-Erniedriger, Schauminhibitoren, Haftfestigkeitsverbesserer und weitere Additive für Kühlschmierstoffe und Konservierung-Wirkstoffe.

Neben den grundsätzlichen Betrachtungen zum Einsatz von Additiven werden ausführlich die Wirkungsmechanismen behandelt. Auch die Bedeutung der Grundöle sowie die Wechselbeziehungen zwischen Grundölen und Additiven nehmen einen breiten Raum. Das Buch schließt mit einem Kapitel über die Analytik der Additive in Schmierstoffen.

Alle Kapitel wurden von namhaften Fachleuten der Additiv- und Schmierstoffindustrie verfaßt.

CHEREMISINOFF N.P. (Ed.), *Elastomer Technology Handbook*. CRC Press, Boca Raton, Ann Arbor, London, Tokyo, 1993, 1096 pp.

The volume provides a more fundamental treatment of concepts and general principles in the design, fabrication, and uses of synthetic elastomers. As a point of clasification, the terms rubber and elastomer are used interchangeably.

It is worth mentioning that this handbook represents the contribution of over forty specialists and consists of informations obtained from authentic and highly regarded sources. It also represents the efforts of scores of engineers and associates who provided advice and consultation in the organization of this volume.

The handbook contains 29 chapters, each one written by known specialists in the field. The parts of the book refer to characterization of polymers, mechanical properties of polymers, interpenetrating polymer networks, thermoplastic elastomers, epoxidized rubbers, polymer blends, processing of elastomers, adhesive aspects of elastomeric materials and polymer applications in the construction industry, e.g. polymer-concrete composites or polymers for solar energy applications.

The reader can find also brief informations about widely used rubber and elastomers, about polymerization basics and butyl rubber polymerization.

The book ends with an alphabetical subject index.

It is felt that this volume will be useful to both the researchers and the practitioners.

Victor Bulacovschi

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ELEONORA DIACONESCU
1917–1994

Le 12 août 1994 nous a quitté pour toujours le maître de conférences Eleonora D i a c o n e s c u, qui a été cadre didactique de l'Université Technique „Gh. Asachi" de Jassy, où elle a travaillé avec dévouement et compétence 35 années.

Eleonora D i a c o n e s c u est née dans la ville de Fălticeni, département Suceava, le 10 mars 1917; ses parents ont été des gens modestes et travailleurs. Elle a fréquenté l'école primaire dans la localité de naissance entre 1924–1928 et ensuite a commencé les études au gymnase de la même ville, dans la période 1928–1932 et les a continué à Suceava, où elle a fréquenté les classes supérieures du lycée pour les jeunes filles „Doamna Maria", pendant la période 1932–1936. Elle a soutenu l'examen de bacalauréat en 1936 et dans la même année se fait inscrire à l'Université „Al.I.Cuza" de Jassy, en suivant les cours de la Faculté de Physico-Chimie.

Comme étudiante elle a fréquenté les cours des quelques professeurs de grande autorité et compétence professionelle à savoir: N. C o s t ă c h e s c u, P. B o g d a n, Radu C e r n ă t e s c u, C. V. G h e o r g h i u, Cristea N i c u l e s c u - O t i n, Gh. A l e x a, I. C i o c h i n ă.

Pendant les études, Eleonora D i a c o n e s c u a travaillé avec assiduité et dévouement, en assimilant des connaissances nécessaires pour devenir une bonne spécialiste. À la fin des études universitaires, en 1940, Eleonora D i a c o n e s c u a travaillé, pour une courte période, comme chimiste à la fabrique de sucre de Iţcani, Suceava, et plus tard, à partir du 1-er juillet 1941 jusqu'au mois d'avril 1942, comme chimiste à la fabrique de draperie de Buhuşi, Bacău.

En avril 1942 elle s'est mariée avec l'ingénieur Vasile D i a c o n e s c u, cadre didactique universitaire à l'École Polytechnique de Jassy.

En 1942 Eleonora D i a c o n e s c u a occupé, par concours, un poste d'assistant universitaire à la chaire de Technologie Chimique des Substances Anorganiques de la Faculté de Chimie Industrielle de l'École Polytechnique „Gh.Asachi", qui en ce temps-la était à Cernăuţi; en conséquence, à partir du 1-er octobre 1942 elle a commencé la carrière didactique universitaire.

En cette qualité, d'assistant universitaire, elle a conduit avec compétence et habileté les travaux de laboratoire de la discipline de Technologie Chimique Générale, dont le titulaire était le professeur dr.ing. M. D i m a (1899–1982).

Pendant l'année 1950 Eleonora D i a c o n e s c u a été avancée maître assistante et en 1952 a été nommée lecteur, ayant comme charge d'enseigner les cours de technologie chimique générale et chimie générale, sections du soir. En 1962 elle a été promue, par concours, au grade didactique de maître de conférences, dans le cadre de la chaire de Chimie générale et au mois de mai 1965 la commission supérieure de diplômes du Ministère de l'Enseignement a attesté son titre.

En cette qualité, elle a enseigné le cours de Chimie générale à la Faculté de Mécanique et, également, le cours de Matériaux de constructions pour la Faculté de Hydrotechnique. Ces disciplines universitaires ont été servies par Eleonora D i a c o n e s c u jusqu'à sa retraite, en 1977.

Ses anciens étudiants ont apprécié toujours la clarté des ses explications, leur caractère didactique et surtout la volonté de la spécialiste de mieux former les prochains ingénieurs.

Dans les entreprises chimiques et également dans celles de profil mécanique ont travaillé et travaillent encore aujourd'hui un grand nombre d'ingénieurs qui ont reçu et assimilé les premières connaissances de chimie et de technologie chimique de Eleonora D i a c o n e s c u.

Ses anciens étudiants ne peuvent pas oublier l'esprit de compréhension et bienveillance, autant que ses bons conseils donnés avec affection et soin, soit comme dirigeant de groupe et de l'année-d'étude ou bien dans sa qualité de directrice éducative.

Parallèlement avec l'activité didactique, Eleonora D i a c o n e s c u a déployé également un fructueux travail de recherches scientifiques, en manifestant aussi dans cette direction initiative et persévérance. Elle a élaboré des travaux scientifiques dans le domaine des échanges de ions, des charbons de terre, des bentonites, ainsi que dans celui de la mise en valeur par voie chimique de quelques matières premières végétales. Elle a contribué également à la connaissance de la composition chimique du roseau et à sa utilisation.

Par son activité didactique, par son énergie et par son travail, ainsi que par ses manières distinguées, elle a gagné l'appréciation de tous ceux qui l'ont connue.

Son décès prématuré représente une douloureuse perte pour l'enseignement chimique supérieur de Roumanie.

Tous qui l'ont connue, cadres didactiques de l'Université Technique de Jassy et également d'autres universités, le corps administratif, étudiants, collègues, ainsi que les ingénieurs et spécialistes qui travaillent dans les usines se rappeleront toujours de Eleonora D i a c o n e s c u avec les meilleurs sentiments de respect et gratitude.

Prof.dr.ing. Savel Ifrim

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